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TECHNICAL SECTION

TECHNICAL TOPICS

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Technical Topics Scheduled for February

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Experimental Studies of Cathodic Protection of Naval Vessels by L. J. Waldron, M. H. Peterson and M. C. Bloom

Applications of Lead-Acid Brick Systems in Chemical Plants by E. J. Mullarkey

THIS MONTH'S COVER—The top of this domestic air conditioner heat exchanger is encrusted with calcium salts deeply stained with blue corrosion products from the copper tube return bends. Extensive corrosion damage has been suffered by the copper lines of this exchanger after about 14 months' operation in the Gulf Coast area.

☆

Directory of NACE Technical Committee Officers

T1   Corrosion in Oil and Gas Well Equipment

Jack L. Battle, Chairman; Humble Oil & Refining Co., P. O. Box 2180, Houston, Texas

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T-1B Condensate Well Corrosion
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T-1B-1 High Pressure Well Completion and Corrosion Mitigation Procedure
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T-1C Sweet Oil Well Corrosion
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T-1C-1 Water Dependent Corrosion, Field Practices
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T-1C-2 Water Dependent Corrosion, Experimental Aspects

T-1C-5 East Texas Task Group
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T-1D Sour Oil Well Corrosion
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T-1F-2 Sweet Crude and Sweet Condensate Stress Corrosion Cracking
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T-1K-1 Sour Crude Inhibitor Evaluation
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T-1K-3 Inhibitor Testing at Elevated Temperatures
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T-1M Corrosion of Oil and Gas Well Producing Equipment in Offshore Installations
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T-1M-1 Offshore Corrosion Control Programs

T-1M-2 Non-Ferrous Construction Materials
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T-1M-3 Cathodic Protection Methods Review
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T2   Pipe Line Corrosion

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T-2B-1 Sources of Impressed Current for Anodes
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T-2B-4 Use of High Silicon Cast Iron for Anodes

T-2B-5 Use of Platinum, Palladium, etc. for Anodes
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T-2C-2 Coupons, As A Criteria For Cathodic Protection
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T-2C-3 History

T-2C-4 Cathodic Protection Criteria Research
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T-2D-2 Inaccessible Locations, Such as Water Crossings
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T-2D-3 Parallel Lines
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T-2D-5 Pipe Observed to Be in a Stray Current Field
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T-2H-2 Criteria to Be Used in Reporting on and Evaluating the Performance of Asphalt-Type Pipe Coatings
C. E. Lee, Chairman; Southern California Gas Co., Box 3249, Terminal Annex, Los Angeles 54, Cal.

T-2H-3 To Assemble and Present Service Histories of Asphalt-Type Pipe Coatings

T-2H-4 Asphalt-Type Internal Coating for Pipe Lines
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T-2H-5 To Review and Encourage Publication of Technical Articles on Asphalt-Type Protective Coatings
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T-2J Wrappers for Underground Pipe Line Coating
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T-2J-1 Asbestos Felt

T-2J-2 Glass Wrap

T-2J-3 Glass Base Outer Wrap
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T-2K Prefabricated Plastic Film for Pipe Line Coating
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Directory of NACE Technical Committee Officers

(Continued From Page 6)

T-2K-3 History and Results
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T-3A-1 General Theory of the Action of Corrosion Inhibitors
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T-3A-2 Methods of Testing & Screening Corrosion Inhibitors
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T-3D-1 Electrical Holiday Inspection of Coatings
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T-3E-2 Corrosion in Railroad Hopper Cars
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T-3G-2 Cathodic Protection of Heat Exchangers
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T-4A Effects of Electrical Grounding on Corrosion
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T-4B-1 Lead and Other Metallic Sheaths
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T-4B-2 Cathodic Protection
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T-4B-3 Tests and Surveys
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T-4E-1 Hot Water Tank Corrosion
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T-5A-3 Acetic Acid
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T-5A-4 Chlorine
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T-5C Corrosion by Cooling Waters

T-5C-1 Corrosion by Cooling Waters (South Central Region)
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T-5D-1 Questionnaires
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Anode notes from National Carbon Company
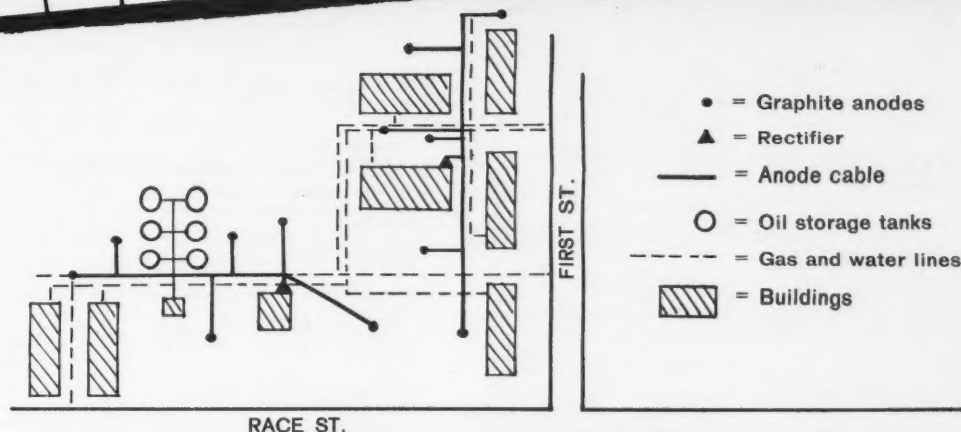
- = Graphite anodes
▲ = Rectifier
— = Anode cable
○ = Oil storage tanks
- - - = Gas and water lines
▨ = Buildings

FIRST ST.

RACE ST.

PROTECTION OF "IN PLANT" UNDERGROUND PIPING AND TANK BOTTOMS

The corrosion engineer of a large industrial products manufacturer with underground gas and water lines spread throughout a plant area of approximately 15 acres, was concerned with mounting maintenance costs. After a corrosion survey he decided to install an impressed current cathodic protection system with "National" Graphite Anodes and Carbonaceous Backfill.

In 1951, six inch and eight inch water lines were bonded to four inch gas lines and to six 25 foot diameter oil storage tanks. These in turn were connected to the negative sides of two 25 amp rectifiers. A distributed anode bed with six 2" x 80" graphite anodes installed in vertical holes 12" diameter with carbonaceous backfill was connected to the positive side of each rectifier. The underground pipe lines and tank bottoms were brought to a minimum pipe to $CuSO_4$ half cell potential of .85 volts with a current output approximately 15 amps and 22 volts per rectifier. Later as the metal became polarized this current was reduced. In 1953, an additional graphite anode was installed to take care of stray currents coming from a railroad spur.

The impressed current cathodic protection system using "National" Graphite Anodes is still in operation, and the corrosion engineer advises that there has been a substantial reduction in the maintenance cost of their underground plant, which more than justified the cost of the installation.
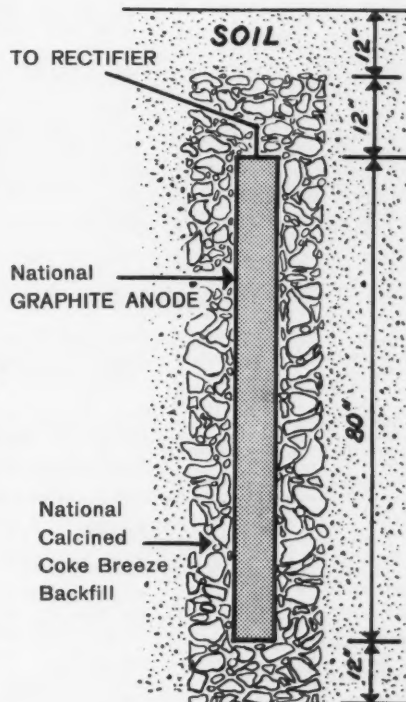
SOIL

TO RECTIFIER

12"

12"

National GRAPHITE ANODE

80"

National Calcined Coke Breeze Backfill

12"

Directory of NACE Technical Committee Officers

T-5D-2 Inorganic Acids
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T-5D-8 Methods and Criteria for Evaluating Plastics in Chemical Environment
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T-5E Stress Corrosion Cracking of Austenitic Stainless Steel
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T6 Protective Coatings

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T-6A-3 Vinylidene Chloride Polymers
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T-6A-5 Polyethylene
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T-6A-6 Neoprene
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T-6A-7 Thermosetting Coal Tar Coatings
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T-6A-9 Furanes

T-6A-10 Polyesters
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T-6A-11 Epoxys
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T-6A-12 Fluorocarbons

T-6A-13 Chlorinated Rubbers
Appointment Pending

T-6A-14 Organic-Brick Covered

T-6A-15 Rigid Vinyls
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T-6A-16 Coal Tar Coatings

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T-9D Correlation of Evaluation of Preservatives

Walter Bejuki, Chairman; National Academy of Sciences, National Research Council, 2101 Constitution Ave., Washington 25, D. C.

TECHNICAL PAPERS SCHEDULED FOR FEBRUARY PUBLICATION

Uses for Varistors With Direct Current Corrosion Meters by W. Searle Woodward

Effect of Molten Boron Oxide on Selected High Temperature Alloys by David Roller and C. R. Andrews

Developments in Cooling Tower System Treatments — Polyvalent Ion — Polyphosphate Inhibitors by J. I. Bregman and T. R. Newman

The Mechanical Properties and Corrosion Resistance of Oil Well Tubing by F. A. Prange

Influence of Service Temperature on the Resistance of Wrought Aluminum—Magnesium Alloys to Corrosion by E. H. Dix, Jr., W. A. Anderson and M. Byron

A Contribution to the Electrochemistry of Some Aluminum Alloys by E. M. Khairy and M. Kamal Hussein

Interaction, A Cause and a Cure by H. C. Bowen, C. Groot and J. L. Jaech

Note on Behaviour of AZ63 Alloy and Magnesium 1% Mn Alloy Anodes in NaCl Electrolyte by J. H. Greenblatt and E. Zinck

Corrosion Activity of Soil by N. D. Tomashov and Y. N. Mikhailovsky

Well Completion and Corrosion Control of High Pressure Gas Wells. A Status Report of NACE Task Group T-1B-1 W. F. Oxford, Jr., chairman

Chloride Stress Corrosion Cracking of Austenitic Stainless Steel—A contribution to the work of Technical Group T-8 on Refinery Industry Corrosion through efforts of Task Group T-8A on Chemical Cleaning by J. P. Engle, G. L. Floyd and R. B. Rosene

Topic of the Month

Corrosion of Valve Seat Ring Results in Flexible Metal

By J. E. PRIOR*

Abstract

Failure occurred in a Type 316 stainless steel valve seat ring after nine months' service in a water treating system. Visual examination showed the ring had suffered intergranular corrosion after exposure to dilute sulfuric acid. The ring also had a high degree of flexibility.

It is believed that the casting was not given the normal homogenizing heat treatment required to properly diffuse the alloying elements throughout the casting.

7.2

THE IMPORTANCE of proper heat treatment of stainless steel components to assure optimum corrosion resistance was demonstrated by the failure of a cast stainless steel, ACI CF12M (Type 316) valve seat ring from a 5-inch gate valve. This valve was used in a water treating system and was subjected to dilute sulfuric acid. It failed after approximately nine months of service.

Visual examination showed that the ring had suffered intergranular corrosion attack. A segment of the ring is shown in Figure 1. It will be seen that some surface grains have fallen out. The ring was not severely corroded in that extensive metal loss was not noted. The threads on the outside diameter of the ring were in fair condition.

The interesting aspect of the attack was the degree of flexibility induced in the corroded ring, as shown in Figure 2.

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This photograph is a quadruple exposure taken with the ring segment held in four different positions, illustrating the flexibility of the material. This metal segment was approximately seven inches long, and the vertical movement from the bottom to the top extreme position was about three inches. The material had a dull, flat ring when struck on a solid object. To the casual observer, the material appeared to have the feel and texture of rubber.

Microscopic examination revealed an almost complete intergranular corrosion attack, with little, if any, bonding remaining between grain boundaries (Figure 3). Apparently the only force holding the metal together was the mechanical interlocking of the grains. Sufficient space remained between the metal grains to permit the ring to move in all directions and give the illusion of flexibility. However, any attempt to force the metal beyond the extreme position shown in Figure 2 resulted in brittle fracture. This fractured surface was dirty and dis-

colored, quite typical of a corroded metal surface.

It is believed that this casting was not given the normal homogenizing heat treatment required to properly diffuse the alloying elements throughout the casting, which would assure optimum corrosion resistance of the cast stainless steel. Although a laboratory curiosity and not likely to recur, this specimen illustrates the importance of proper heat treatment for satisfactory corrosion resistance of stainless steel alloys in corrosive environments.

Figure 1—Segment of valve seat ring. Note areas where grains have fallen out of the surface.
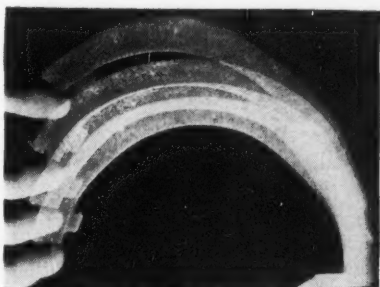
Figure 2—Demonstration of the flexibility of corroded valve seat ring.
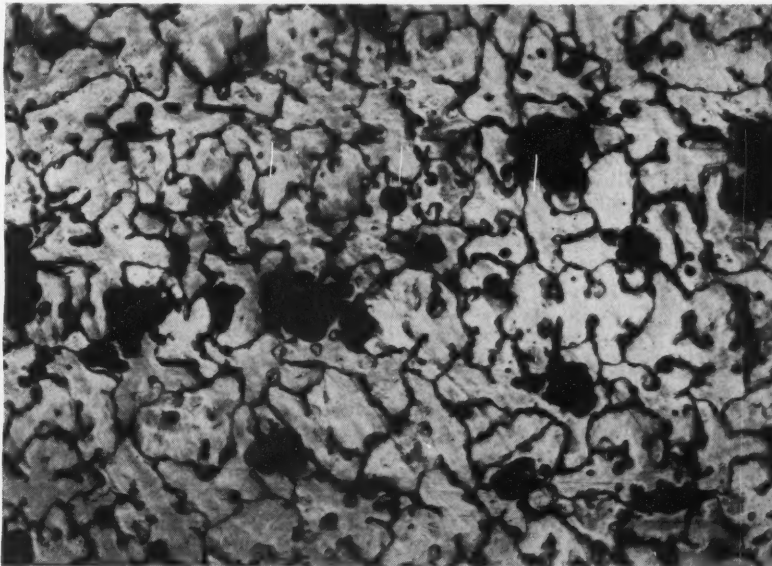
Figure 3—Photomicrograph showing virtually complete intergranular corrosion attack. 100X; marbles reagent etch.

Corrosion of Steel Weldments*

By J. U. MacEWAN and H. H. YATES

Introduction

PREMATURE FAILURE of a welded structure may occur as a direct fracture associated with poor mechanical properties at the weld site. Several factors may contribute to such failure including structural inhomogeneity introduced by temperature cycles in the welding operation or the introduction of gases or particles of oxide and slag into the weld bead.

Advances in welding techniques and testing methods have reduced the occurrence of this type failure. Increased severity of corrosion in the weld area may lead to fast penetration of the metal and premature failure of the structure. Investigation of this aspect of the problem is desirable because the welding operation introduces a number of factors having a detrimental effect on corrosion. These include general chemical and physical heterogeneity with emphasis on the removal or addition of certain critical alloying elements, and porosity or inclusions as noted above, plus heat effects such as stress concentration and modification of grain structure. The literature reveals few studies of this problem with scattered accounts of service behavior of specific materials in specific environments. However, information is accumulating as indicated in the following survey.

Weight loss in total immersion tests in beakers containing 20 percent sulfuric acid at 30 C was found to evaluate primarily parent metal,[1, 2] but visual rating connected increased severity of corrosion with inclusions of oxide or slag which would be eliminated by proper choice of welding rod. Small additions of chromium, copper, manganese, silicon and nickel improved results obtained in alternate immersion tests in beakers containing synthetic sea water at 30 C. Potential measurements between weld metal and parent metal were inadequate to predict corrosion rates, and later discussions of these and other studies at the French Welding Institute[3, 4, 5] stressed the importance of heterogeneity in the behavior of welds.

Hunsicker[6] reported good correlation between potentials measured against the quinhydrone electrode in one percent sodium chloride solution and the corrosion of welds in normal hydrochloric acid for steel, cast iron, aluminum, copper and lead. Increased corrosion was observed with increased grain size, and a later paper[7] relates heat treatment temperatures to grain size and corrosion rate.

Potential measurements[8] between weld metal and parent metal have shown the weld metal to be cathodic in hot alkali

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MacEwan   Yates

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solution and anodic in acid solution at room temperature. The effects of electrode coating, heat treatment, gas bubbles and slag inclusions are also noted. Various welding operations and corrosion behavior are discussed by Pray and co-workers[9] while Kuznetsova[10] notes the effect of electrode coatings.

Almen[11] has reported that welded structures fabricated from ductile steel fail by brittle fracture caused by fatigue, stress corrosion cracking or biaxial tension. Stress corrosion cracking of steel welds is discussed also by Baerlecken and Hirsch[12] and by Karnisky and co-workers.[13] Welding, stress relieving and corrosion are considered by Ferguson[14] in relation to the operation of a chemical plant; Huseby and Scheil[15] report the corrosion resistance of several mild steel welds in sulphate paper digesters. More date are listed in the paper by Radeker.[16] Klosse[17] has demonstrated the importance of sample size in the corrosion testing of steel welds, and Langer[18] describes apparatus for testing welded seams in fast moving sea water.

The corrosion of steel welds and unwelded parent metal in air saturated with moisture at 50 and 75 C depends on welding processes and materials as well as the parent metal.[19] In a study of welded low alloy steels Frumin[20] found manganese steel less resistant than others to air corrosion. No difference was found

Abstract

Forty-six different steel weldments were subjected to 12 months' alternate immersion in 3 percent sodium chloride solution. Weight loss was more dependent on the type of steel than the nature of the weld, but severity of corrosion in the weld region was affected by both factors. Apparatus was constructed to measure short circuit current between exposed surfaces of parent metal and weld metal. Rapid fluctuations in this current made precise determinations difficult, but average values were reproducible if a set conditioning procedure was used prior to measurement. Variations in current with sodium chloride concentration and with oxygen content of a gas mixture bubbled into the solution were determined, and the activation energy in a 3 percent sodium chloride solution increased from 4 to 6 kcal/mole as the oxygen content of the gas mixture decreased from 100 to 20 percent.   3.7.3

for the same steels in water, and in all cases the addition of molybdenum to the welding rod reduced corrosion, presumably by refining the grain size.

Several reports have been published on the corrosion of welded non-ferrous metals during atmospheric exposure,[21] in nitric and sulphuric acids[22] and in numerous industrial chemicals such as motor oil and fuels, solvents, bleach liquors and acids.[23] Koch and Nagel have also reported that aluminum alloys with a short solidification range are less sensitive to weld cracking.[24]

This paper presents the results of a limited survey of the corrosion of welded plain carbon and low alloy steels and describes a technique useful in studying the mechanism of this type of corrosion.

Experimental Techniques and Results

Corrosion Tests

Forty-six different weld specimens were prepared using two mild steels and one low alloy steel in combination with two gas welding rods and seven welding electrodes. Six different types of joints and, in the case of low alloy steel, two preheat temperatures were used. Specimens 3 by ¾ inches with the weld located an inch from one end were cut from plates formed by welding the long edges of two panels 18 by 3 inches each.

Two annealed samples and two unannealed samples of each type were subjected to alternate immersion in 3 percent sodium chloride solution for two 6-months periods. Average weight losses reported in Table 1 do not agree with visual severity ratings based on increased attack at the weld site. The following generalizations, illustrated with photographs of typical specimens, are based on visual examination of all specimens.

1. Increased attack at the weld site occurred in all specimens except 4130* steel welded with E502-15* electrode (Figures 1 and 2).

Figure 1

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D: 20
G: 10
J: 20

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* Steels are referred to by AISI designation and welding materials by AWS specification.

Figure 1—Welded ⅛-inch panels after 12 months' alternate immersion in 3 percent NaCl solution. Approx. 2X.

A: 101812A	B: 101812A*	C: 101815A
D: 201812A	E: 201812A*	F: 201815A
G: 101812B	H: 101812B*	I: 101815B
J: 201812B	K: 201812B*	L: 201815B
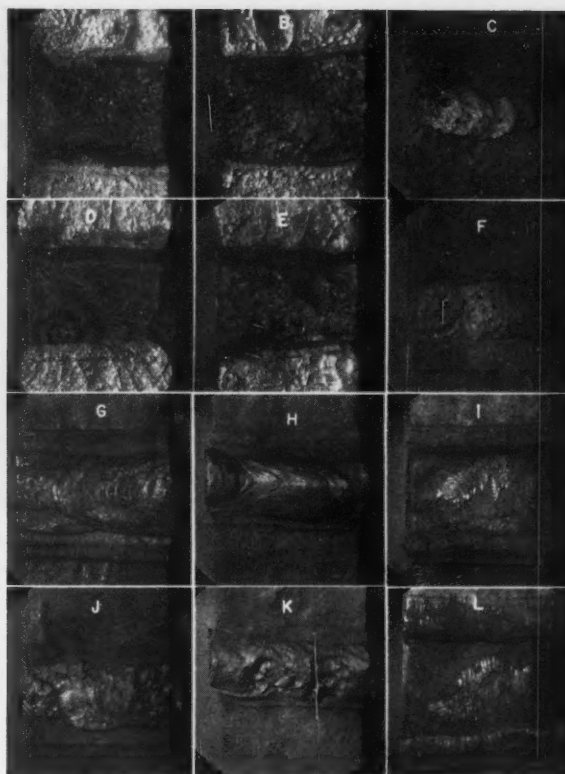
*annealed

Figure 2—Welded ⅛-inch panels after 12 months' alternate immersion in 3 percent NaCl solution. Approx. 2X.

A: 101850E	B: 201850E	C: 301850E
D: 101860E	E: 201860E	F: 301860E
G: 301802A2	H: 301802B6	I: 301890A2
J: 301802A2*	K: 301802B6*	L: 301890A2*

*annealed

2. Adjacent to the weld, 4130 steel developed a protected zone about ⅛-inch wide with electric welding (Figure 2, G-I) and ½-inch wide with gas welding (Figure 2, C and F).

3. Panels of 1020 steel suffered greater attack than equivalent panels of 1010 steel (compare rows 1 and 3 with 2 and 4, Figure 1).

4. Type GA60 welding rod appears to have some advantage over type GA50 (Figure 2, A-F), particularly for welding 4130 steel.

5. Little difference was noted between mild steel electrodes (Figure 1), but E502-15 electrode was better than E9011 electrode for welding low alloy steel (Figure 2, G-I).

6. Annealing improved mild steel panels slightly (Figure 1, columns 1 and 2) but caused deterioration of E502-15 weld bead (Figure 2, J and K).

7. One-quarter inch mild steel panels were attacked less severely than equivalent ⅛-inch panels, possibly caused by heat effects or minor differences in the steel. Corrosion was more uniform as indicated by comparison of Figure 3, A and D with Figure 2, B and E.

Galvanic Experiments

Attempts to obtain reproducible emf values between exposed surfaces of weld metal and parent metal failed. A cyclic variation of about 2 mv with a period of 10 to 15 minutes suggested opposing tendencies to passivation and activation (Figure 4B). Overriding this relatively predictable event was a variation of unpredictable magnitude and period (Figure 4A). In some cases reversal of sign occurred, and the possibility of correlation with corrosion results was remote.

On the other hand, conditions existing at a corroding panel are essentially those of a shorted galvanic cell. Apparatus similar to that described by Godard[25] was used to measure short circuit current between exposed surfaces of parent metal and weld metal (Figure 5). If possible changes are overlooked in the resistance and emf of the corrosion cell with deviations from the short circuit condition, application of Kirchoff's laws gives for the short circuit current $I_C°$

$$I_C° = I_A + I_G\left(1 + \frac{R_G}{R_C}\right)$$

The factor $\left(1 + \frac{R_G}{R_C}\right)$ was approximately 100 for least favorable experiments. Currents in the range of 40 μamp were steady, and the galvanometer was easily balanced within 0.5 mm corresponding to an error of 1 μamp. Higher currents

in the range of 200-400 μamp were less steady giving errors in the order of 5 percent of the reading.

The weld was cut to expose end surfaces of parent metal and weld metal which were filed flat and finished with 00 grade polishing paper. The pieces were then clamped in a lucite holder (Figure 6) with the exposed surfaces face to face with a separation of 5.3 mm. All other metal surfaces were coated with paraffin wax, and electrical contact was made through the clamping screws.

The results using 3 percent sodium chloride solution were extremely sensitive to agitation and oxygen supply and somewhat less sensitive to conditions existing prior to measurement. However, a consistent procedure gave reasonably reproducible results showing sufficient correlation with corrosion to distinguish between good and bad welds. For example, a weld of the type shown in Figure 2H produced 530 μamp/sq cm cathode area (parent metal to weld metal) and the type shown in Figure 1J gave 616 μamp/sq cm cathode area (weld metal to parent metal).

The exposed test surfaces illustrated in Figures 3B and 3E offer further evidence of the definite anode-cathode relationship between weld metal and parent metal for these specimens. On the other
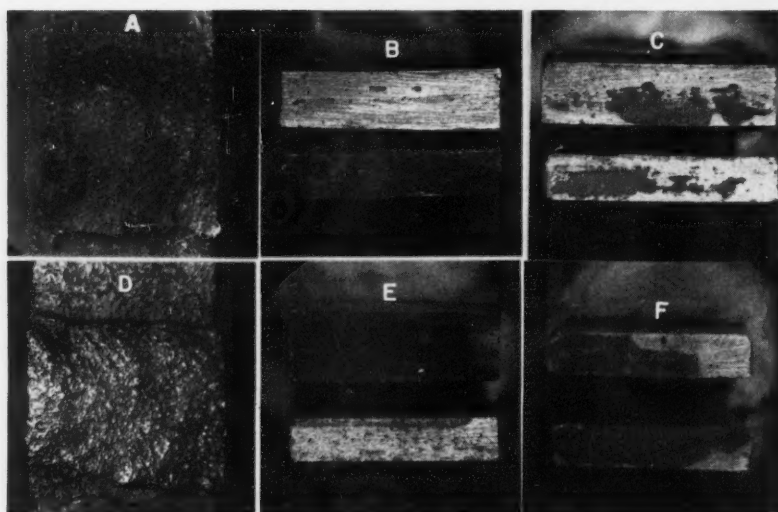
Figure 3—Welded ¼-inch panels after 12 months' alternate immersion in 3 percent NaCl solution. Approx. 2X.
A: 201450F, D: 201460F and exposed surfaces after short circuit test (weld on top), B: 301802B6 annealed,
C: 101815B, E: 201812B, F: matched mild steel surfaces.

Figure 4—Variation of emf between weld metal and parent metal in 3 percent NaCl solution.

Figure 5—Short circuit current apparatus. G—galvanometer, C—corrosion couple, A—ammeter, SR—reversing switch, SS—shorting switch.

hand, the surfaces in Figure 3C show no definite anode-cathode relationship in agreement with the corrosion indicated in Figure 1I. Also the current obtained in this case was smaller (about 75 μamp/sq cm cathode area—weld metal to parent metal) although part of this difference may have been due to a slight difference in conditioning treatment. A current of about 67 μamp/sq cm cathode area was obtained for the matched surfaces of parent metal illustrated in Figure 3F for comparison.

To evaluate the importance of numerous factors controlling these currents (and possibly corrosion), a bubbler was introduced to supply regulated mixtures of oxygen and nitrogen to the solution. The position of the bubbler relative to the sample holder was fixed, and the gas mixture was introduced at a rate (30 ml/min) fast enough to minimize the effect of minor changes in total flow. The surfaces were short circuited and conditioned for 18 hours using a 20 percent oxygen mixture.

The gas was then changed to 100 percent oxygen and maintained until a steady value of current was obtained. The gas was reduced successively to oxygen contents of 80, 60, 45, 20, 10 and 0.3 percent and maintained at each level until the new steady current was obtained. Although erratic with sudden swings to 15 percent, the current fluctuated at a definite level for each new condition. Results for 4130 steel welded with E502-15 electrode are shown in Figure 7 for which the areas of the parent metal and weld metal surfaces were 0.598 and 0.743 sq cm respectively. The effect of sodium chloride in the solution is shown in Figure 8. Current flow in all cases was from parent metal to weld metal.

Activation energy based on current measurements at 25.2 and 40.5 C in a solution containing 3 percent sodium chloride varied with oxygen content of the gas from 4160 cal/mole for pure

oxygen to 5850 cal/mole for the 20 percent oxygen mixture. This variation requires further study before it can be fully accepted. The values are included chiefly to indicate order of magnitude.

Aeration of only one of the surfaces using a filter paper separator always developed cathodic conditions at the aerated surface.

Discussion

The generally accepted electrochemical mechanism of this corrosion process, although not established in detail, involves an anodic reaction such as

$$Fe \rightarrow Fe^{++} + 2e \qquad (1)$$
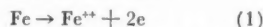
and a cathodic reaction such as

$$2H^+ + 2e \rightarrow H_2 \qquad (2)$$

$$H^+ + 2e + \tfrac{1}{2}O_2 \rightarrow OH^- \qquad (3)$$
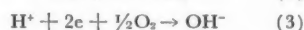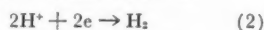
For iron and steel, reaction (2) occurs only in acid solution; in sodium chloride solution corrosion proceeds predominantly by reaction (3). A secondary reaction

$$2Fe^{++} + 4OH^- + H_2O + \tfrac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \qquad (4)$$

produces ferric hydroxide which precipitates partly on the anode surface as a rust layer and partly in the solution as a flocculent dispersed phase.

The tendency for a surface to be definitely anodic or cathodic (Figure 3, B and E) would indicate a minimum of local cell action so that the corrosion rate in equiv/sq cm sec should be given by I/AF where I is the current in amp, A the area in sq cm and F the faraday. If the anode reaction is of interest (rate of penetration), the anode area is used; if the cathode reaction is of interest (rate of oxygen supply), the cathode area is used. On this basis, the reaction velocity corresponding to the maximum current of 430 μamp would be 0.0216 me/sq cm hr cathode area or 0.0268 me/sq cm hr anode area. The average
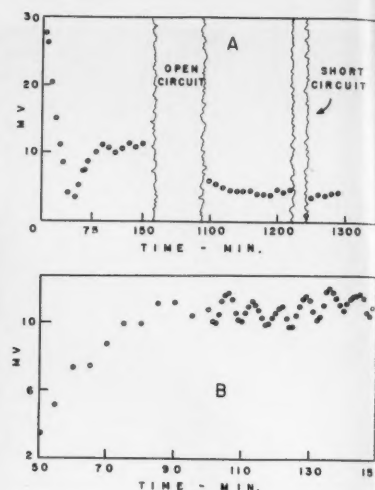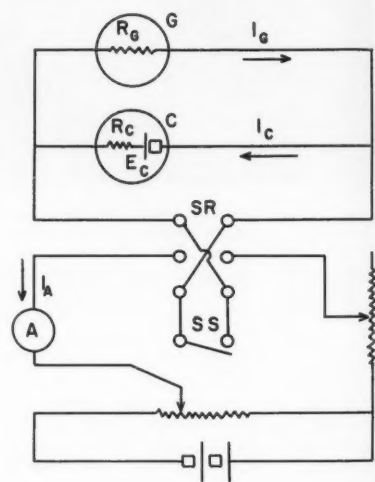
corrosion rate based on total exposed area would be 0.0119 me/sq cm hr (0.152 inch/yr penetration). This is about three times the rate given by LaQue[26] for the corrosion of steel in fast moving sea water. If the current corresponding to a gas mixture containing 20 percent oxygen is used, the penetration rate is reduced to 0.044 inch/yr which is within the limits quoted by LaQue.

The discrepancy between weight loss (Table 1) reported for the weld shown in Figure 1I and the low current obtained with this sample is readily explained by the appearance of the exposed surfaces in Figure 3C. The galvanic effect in this case was not enough to prevent local cell action so that anode areas developed on both surfaces. Much of the corrosion current did not pass through the external measuring circuit. Further insight into corrosion behavior

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TABLE 1—Weight Loss in gm/sq dm After Twelve Months' Exposure

Sample No.	Electrode or Rod	Joint*	Preheat, Degrees F.	Weight Loss
One-eighth Inch AISI 1010 Steel Samples				
101810A	E6010	A	—	69
101811A	E6011	A	—	66
101812A	E6012	A	—	69
101815A	E7015	A	—	60
101820A	E6020	A	—	69
101810B	E6010	B	—	69
101811B	E6011	B	—	68
101812B	E6012	B	—	71
101815B	E7015	B	—	68
101820B	E6020	B	—	70
101850E	GA50	E	—	66
101860E	GA60	E	—	66
One-eighth Inch AISI 1020 Steel Samples				
201810A	E6010	A	—	74
201811A	E6011	A	—	74
201812A	E6012	A	—	71
201815A	E7015	A	—	67
201820A	E6020	A	—	68
201810B	E6010	B	—	74
201811B	E6011	B	—	75
201812B	E6012	B	—	82
201815B	E6015	B	—	80
201820B	E6020	B	—	81
201850E	GA50	E	—	69
201860E	GA60	E	—	73
One-quarter Inch AISI 1020 Steel Samples				
201410C	E6010	C	—	62
201411C	E6011	C	—	66
201412C	E6012	C	—	66
201415C	E7015	C	—	67
201420C	E6020	C	—	66
201410D	E6010	D	—	67
201411D	E6011	D	—	65
201412D	E6012	D	—	66
201415D	E7015	D	—	66
201420D	E6020	D	—	67
201450F	GA50	F	—	72
201460F	GA60	F	—	73
One-eighth Inch AISI 4130 Steel Samples				
301802A2	E502-15	A	200	57
301802A6	E502-15	A	600	61
301890A2	E9011	A	200	66
301890A6	E9011	A	600	70
301802B2	E502-15	B	200	63
301802B6	E502-15	B	600	57
301890B2	E9011	B	200	64
301890B6	E9011	B	600	58
301850E	GA50	E	—	57
301860E	GA60	E	—	55

* Types of Joints

Joint	No. of Passes	Gap. in.	Back-up Strip	Bevel Angle
A	1	1/16	Yes	0
B	2	0	No	0
C	1	1/8	Yes	60
D	2	1/8	Yes	60
E	1	3/32	No	0
F	2	0	No	60

Figure 6—Lucite couple holder. S—Specimen, C—clamping screws.
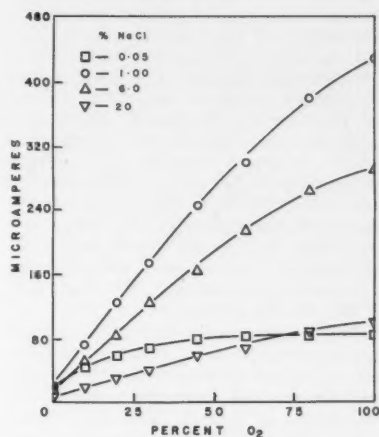
Figure 7—Variation of short circuit current with O₂ content of bubbled gas for various sodium chloride concentrations.
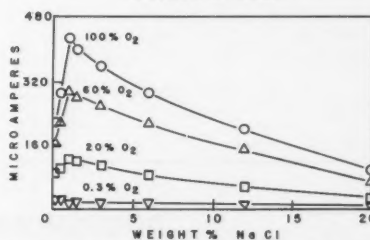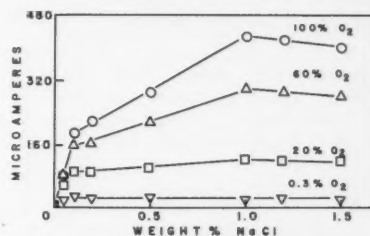
Figure 8—Variation of short circuit current with sodium chloride concentration in the solution for various gas mixtures.

of this type may be obtained by considering the results in terms of chemical kinetics. Solid-liquid reactions controlled by diffusion of a dissolved reactant gas through the diffusion layer to the solid surface have been considered by Halpern[?] giving a maximum rate of 0.001 mole/sq cm hr for a well agitated system and a gas solubility of 0.01 mole/1. Where oxygen is required at the cathode surface according to reaction (3), this corresponds to 4 me/sq cm hr which is considerably greater than the value of

0.0216 noted earlier. However, the solubility of oxygen in sodium chloride solutions of approximately 1 percent appears to be closer to 10^{-3} mole/1 or less.[25] This would reduce the maximum rate from 4 to 0.4 me/sq cm hr. The remaining difference is partly associated with insufficient agitation for maximum current (the bubbler was horizontally displaced about 2 cm from the reaction surfaces). The low corrosion rate may also result, as suggested in the following paragraphs,

from a slow stage involving the chloride ion which is still effective in this region.

The effects of oxygen and chloride shown in Figure 8 are similar to the effect of ammonia and oxygen in the solution of copper reported by Halpern[29] and explained on the basis of slow diffusion of ammonia or oxygen to the reacting surface. It is proposed that the solution of iron (steel) in sodium chloride solution involves both oxygen and chloride ion. Oxygen is used at the cathode

surface for reaction (3) as suggested by its effect in the two compartment cell. Chloride ion is used at the anode surface, probably in secondary reactions yielding precipitated ferric hydroxide. Adsorption of chloride ion by colloidal particles of ferric hydroxide is mentioned by Akimov[30] and could affect the precipitation process itself. The results in Figure 8 can be explained as follows:

At salt concentrations below 0.1 percent, diffusion of chloride ion is rate controlling and oxygen content of the gas has little effect. Curves for all oxygen contents coincide in this region, but the current rises rapidly with percent sodium chloride. For salt concentrations above 0.1 percent and oxygen contents below 20 percent, diffusion of oxygen is rate controlling giving the horizontal portions of these curves. At higher oxygen contents, salt concentration also has an effect which increases steadily with oxygen content up to 100 percent. The effect of salt concentration in this region is much less pronounced than at the lower levels and may be due to mixed control by diffusion of both oxygen and chloride. Changes in conductance also may play a role in this region.

When sodium chloride is present at concentrations above 1.0 percent, solubility of oxygen in the solution is reduced and the reaction velocity decreased. The occurrence of a sharp maximum in current at 1 percent sodium chloride differs from corrosion results reported by Borgmann[31] for 48-hour partial immersion tests. These results show a broad maximum at about 0.4 N (approximately 2.3 percent) with little decrease to 0.25 N

(approximately 1.4 percent). The deviation is not large and may be the result of different surface conditions; separate surfaces used for current measurement leave the cathode free from rust and accessible to oxygen at all times. Thus the increase in current obtained with separate surfaces as salt concentration is reduced from 2.3 to 1.0 percent may be counteracted in the corrosion of a single surface by the formation of an increasingly protective rust film over the whole with attendant curtailment of oxygen supply.

The activation energy in 3 percent sodium chloride solution is only slightly greater than values quoted for diffusion controlled processes of this type. Several possible explanations exist for its variation with oxygen content of the gas, but detailed consideration of this aspect of the problem must await further investigation.

Although the short circuit current technique is not applicable to general corrosion studies, its simplicity and speed offer definite advantage for preliminary evaluation of the galvanic behavior of two different metal surfaces in contact if they can be separated for testing. Solution variables and other conditions of service can be studied with ease as well as the action of inhibitors and accelerators.

Even though results may not correlate with the reactions that could be expected from corrosion theory in many instances, additional information concerning the mechanisms involved should help to improve methods of combatting corrosion losses.

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High Temperature Corrosion Product Films on Aluminum*

By V. H. TROUTNER

Introduction

MOST ALUMINUM alloys corrode in high purity water at high temperatures (above 150 C) in a uniform manner which follows a parabolic rate law. After an induction time, the process changes to a more severe form of corrosion which obeys a linear rate law. The duration of the induction time is dependent on the alloy composition and decreases rapidly with increasing temperature. Because the uniform parabolic corrosion process is controlled by the corrosion product film,[1] a change must occur in the film which permits the change in corrosion mechanism to give the linear process.

This paper investigates corrosion product films by means of electron microscopy to detect any changes which might occur in their structure. Films formed on aluminum in corrosion inhibitors were also examined.

Experimental Data

Aluminum alloys 1245 and X-8001 were used. The compositions are given in Table 1. The uniform corrosion rates of both alloys are the same. The induction time of 1245 alloy is much shorter than that of X-8001. Corrosion product films were formed on the aluminum coupons by exposure in static autoclaves. Short exposure times were obtained by induction heating the autoclaves.

The outer surface of corrosion product films were replicated by a standard examination technique for electron microscope. A cellulose acetate replica was prepared directly from the surface of the corroded specimen. This was shadowed with palladium and coated with carbon in a vacuum evaporator unit. The replica was cut into 1/8-inch squares, and the plastic was dissolved in a dish of acetone. The palladium shadowed carbon replicas were mounted on 200-mesh specimen grids for examination.

A procedure was developed for replicating the inner surface of the corrosion product films, that is, the surface of the film adjacent to the metal. The steps in this procedure are outlined in Figure 1. A corroded specimen was mounted in a block of cold setting resin (Thalco Boat Resin). The mounted specimen was ground to expose the aluminum. The aluminum was dissolved in a warm iodine-methanol bath[2] leaving the corrosion product film mounted with its inner surface exposed. Palladium shadowing and carbon deposition were applied directly to the exposed inner surface of the film. A foil mask was used to restrict

the palladium and carbon deposit to the corrosion product surface. The coated area was scored with a knife into 1/8-inch squares. The resin block was then placed in a beaker of 50 weight percent phosphoric acid and heated for an hour in a pressure cooker at 5 psig. The phosphoric acid dissolved the corrosion product and permitted fragments of the carbon replica to float free. The replica fragments were removed from the phosphoric acid by means of a spoon made of stainless steel fine mesh screen. The fragments were rinsed by floating in a dish of distilled water after which they were mounted on a specimen grid for examination.
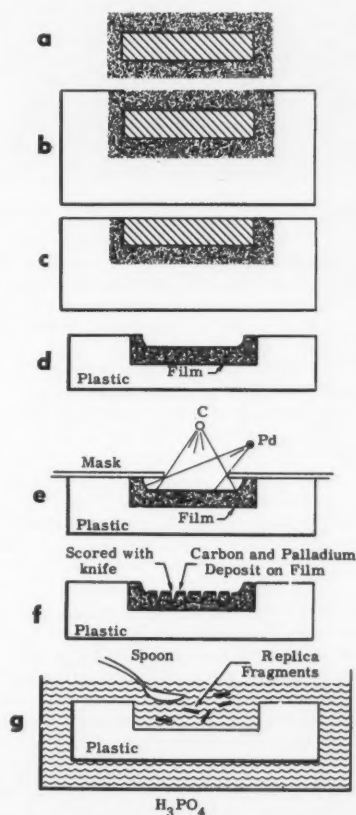
Figure 1—Procedure for preparing replicas of inner surface of corrosion product films: (a) Corroded aluminum sample. (b) Sample mounted in cold setting plastic (boat resin). (c) Sample ground off to remove top layer of corrosion product and to expose metal. (d) Metal removed in iodine-methanol bath leaving mounted corrosion product film with inner surface exposed. (e) Sample masked, shadowed with palladium and deposited with carbon. (f) Sample scored through carbon deposit and corrosion product. (g) Corrosion product dissolved in hot H_2PO_4 permitting carbon replicas to float free where they are collected with stainless mesh spoon.

Abstract

The corrosion product films formed on aluminum in aqueous environments at high temperatures have been examined with the electron microscope. A technique is described for the preparation of electron microscope replicas of the surface of the corrosion product films adjacent to the metal. Electron micrographs are shown of corrosion product films formed during various stages of corrosion in high purity water, and in corrosion inhibited systems. Corrosion inhibition was found to be associated with different crystalline structures of the corrosion product films.   2.3.6

Discussion of Results

Samples of 1245 and X-8001 alloys were exposed to high purity water at 310 C for 2, 5, 10, 20 and 40 minutes. The corrosion curves are shown in Figure 2. The 1245 samples taken at 2 and 5 minutes were corroding by the uniform process. The 20 and 40 minute samples were corroding by the more severe linear process. The 10 minute sample was taken during the change of corrosion processes. All the X-8001 samples were corroding uniformly.

Figure 3 shows the typical outer film surface formed on X-8001. The surfaces were composed of crystals of uniform size and distribution. The size of the crystals gradually increased with increasing time of exposure. Figure 4 is typical of all the X-8001 inner film surfaces. They were all amorphous in appearance and showed walls which corresponded to penetration into the grain boundaries of the metal.

Figures 5 and 6 show typical results obtained with films formed on 1245 alloy. The outer surfaces were crystalline, but crystal size and distribution were erratic. Crystal size gradually increased with increasing exposure. The inner sur-
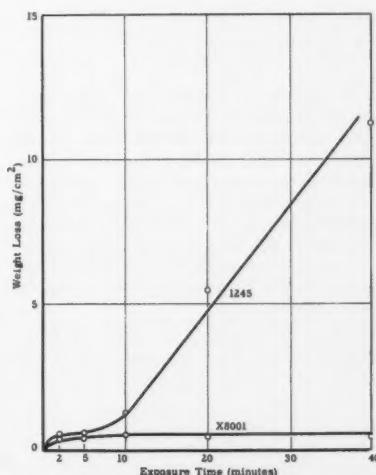
Figure 2—Weight losses of 1245 and X-8001 aluminum alloys at 310 C in water.
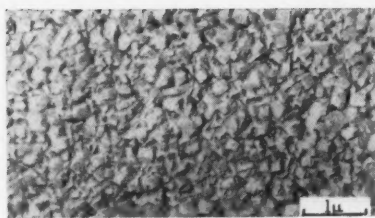
Figure 3—Outer surface of X-8001 film.
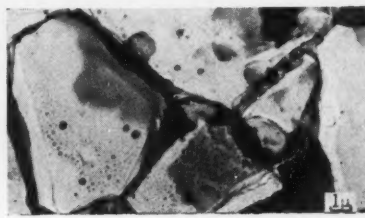
Figure 4—Inner surface of X-8001 film.
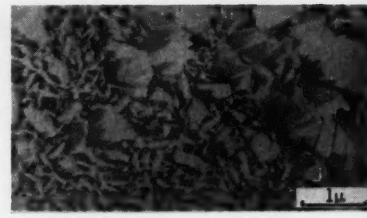
Figure 5—Outer surface of 1245 film.
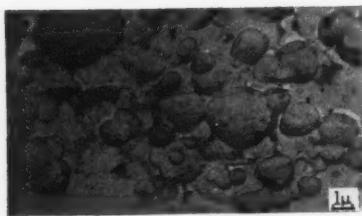
Figure 6—Inner surface of 1245 film.
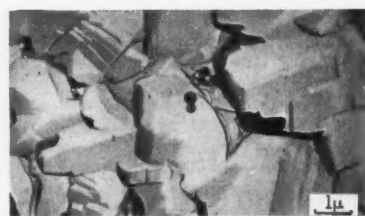
Figure 7—Outer surface of corrosion product film.
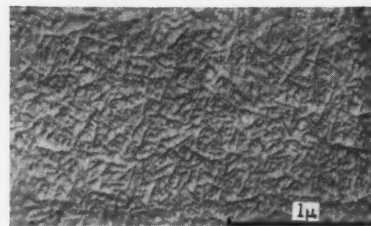
Figure 8—Outer surface of chromic acid film.
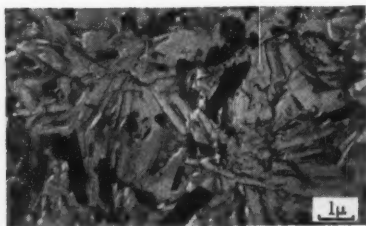
Figure 9—Outer surface of film formed at 180 C in pH 4 phosphoric acid.
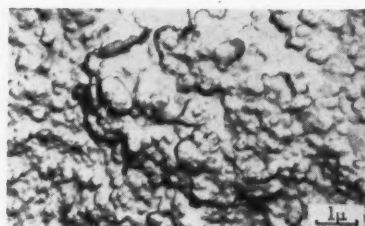
Figure 10—Inner surface of film formed at 180 C in pH 4 phosphoric acid.

Figure 11—Outer surface of film formed at 300 C in pH 4.5 phosphoric acid.

TABLE 1—Composition of Aluminum Alloys

Alloy 1245				Alloy X-8001 (formerly M-388)	
Element	Percent	Element	Percent	Element	Percent
Al	99.45*	Ti	0.03	Al	97.51*
Fe + Si	0.55**	Bi	0.01	Cu	0.15**
Fe/Si	2	Pb	0.01	Li	0.008**
Cu	0.04**	Sn	0.01	Cd	0.003**
Mn	0.03**	Li	0.008	Co	0.001**
Mg	0.01**	Cd	0.003	B	0.001**
Cr	0.03**	B	0.001	Ni	0.9-1.3
Ni	0.01**	Co	0.001	Fe	0.45-0.70
Zn	0.03**			Si	0.17**
				Others	0.5 each or 0.15 total

* Minimum percentage
** Maximum percentage

faces appeared amorphous. The walls which appeared on the X-8001 inner film surfaces were found also on the 1245 inner film surfaces at all exposure times. They were found to be amorphous to x-rays. These walls, or grain boundary penetrations, were observed optically. Because of the relatively large grain size of the 1245 samples, the walls did not appear in the high magnification electron micrographs.

Figure 7 is typical of both 1245 and X-8001 after long exposures at high temperatures. The corrosion product film has been characterized by x-ray diffraction as Boehmite, $Al_2O_3 \cdot H_2O$. No structural changes were observed in the corrosion product films associated with the change from uniform corrosion to the more severe linear corrosion.

The film formed on aluminum by autoclaving in one percent chromic acid at 170 C for 40 hours inhibits corrosion. The film is very thin and is amorphous to x-rays. Figure 8 shows the outer surface of this film at high magnification.

It is uniform and has very small crystal size.

The presence of phosphate at low concentration inhibits aluminum corrosion. The corrosion product has been characterized by x-ray diffraction as Augelite, $2 Al_2O_3 \cdot P_2O_5 \cdot 3H_2O$. The film formed on X-8001 at 180 C in pH 4 phosphoric acid is shown in Figures 9 and 10. This crystal structure has also been found at 200 and 250 C. At 300 C in pH 4.5 phosphoric acid, the film formed is Boehmite as shown in Figure 11 and as verified by x-ray diffraction. Since the Augelite film was not formed, it is doubtful whether there was any phosphate inhibition at this temperature and pH.

Acknowledgment

The electron micrographs were taken by B. Mastel of the Hanford Laboratory Operation.

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Any discussions of this article not published above will appear in the June, 1959 issue

**Part 1—Role of the Corrosion Product Film
In the Uniform Aqueous Corrosion of Aluminum★**

Observations on the Mechanisms and Kinetics
Of Aqueous Aluminum Corrosion

By V. H. TROUTNER

Introduction

ALUMINUM IS resistant to corrosion because of the formation of a protective film of oxidation or corrosion product. The highly reactive nature of aluminum and the protection offered by the corrosion product film are easily demonstrated by amalgamating the surface of a piece of aluminum with mercury and placing it in water. The mercury prevents the formation of a continuous protective film on the surface of the aluminum and, consequently, the aluminum reacts rapidly and completely with the water. Even with its protective film, aluminum does corrode. As service requirements become more severe, as in high-temperature, high-pressure nuclear reactors, corrosion becomes more of a problem.

In aqueous systems, aluminum corrodes in three distinct ways: by pitting attack, uniform attack, and intergranular attack. Pitting generally occurs at temperatures below 100 C and can be prevented by a few parts per million of sodium dichromate inhibitor. Uniform attack occurs in conjunction with pitting but is of minor significance by comparison. In the intermediate temperature region from about 90 to 250 C, uniform attack is the principal form of corrosion. At elevated temperatures, usually above 250 C, uniform attack is a prelude to the highly destructive intergranular attack.

This paper considers the effect of the

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corrosion product film in the uniform penetration corrosion of aluminum both as the principal form of corrosion and as a prelude to intergranular attack. The effects of solution composition and alloy composition will also be considered.

Duplex Corrosion Product Films

Recently, Hunter and Fowle[1] have shown that, when aluminum is oxidized in air or when it is anodized, a duplex corrosion product film is formed, as illustrated in Figure 1. The film consists of a thin protective barrier film adjacent to the aluminum surface and a more perme-
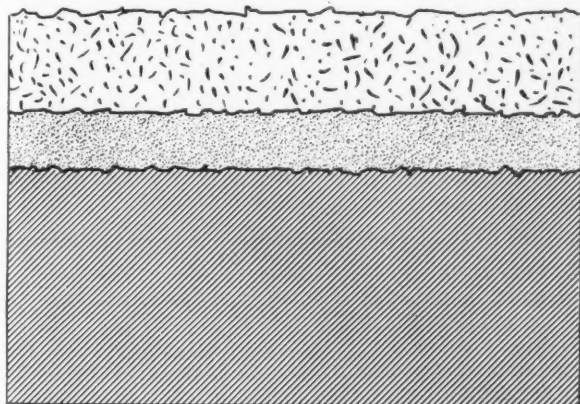
Abstract

Several experiments are discussed from the standpoint of their implications on the role of the corrosion product film formed on aluminum during uniform aqueous corrosion both as the principal form of corrosion and as a prelude to intergranular penetration. The experiments include barrier film measurements, the effect of an applied potential on corroding aluminum, the effect of various ions and combinations of ions in dilute aqueous solutions on the uniform corrosion, x-ray diffraction studies of corrosion product films, and several comparisons between air oxidation studies and aqueous corrosion studies. Conclusions are given on the composition and structure of aluminum corrosion product film and the role it plays in controlling uniform aqueous corrosion.
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able outer bulk film. The thickness of the barrier film was estimated by measuring its breakdown potential. The sample was made the anode in a three percent tartaric acid solution at pH 5.5. The applied voltage is steadily increased and the current is plotted as a function of voltage. The voltage at which the current exceeds the normal leakage current is taken as proportional to the thickness of the barrier film.[2] The barrier film rapidly reaches a maximum thickness which is dependent only upon the temperature of formation and, in the case of anodizing, the applied potential. The maximum barrier thickness was shown to be the same for oxygen, dry air and moist air.

Measurements similar to those of Hunter and Fowle were made on aluminum specimens which were corroded in water at elevated temperatures. It was shown that a barrier film forms in water which reaches the same maximum barrier voltage (and presumably thickness) as in air, dependent only upon the tem-

Figure 1—Cross section of corroded aluminum. Bottom layer is aluminum metal. Top layer of bulk film may grow in thickness with time. Thin middle layer of barrier film grows rapidly to maximum thickness.

Temperature: 125°C
Water: Mixed Tap and Distilled
Sample Area: 51.6 cm²

+ Anode Sample
− Cathode Sample
C Control Sample
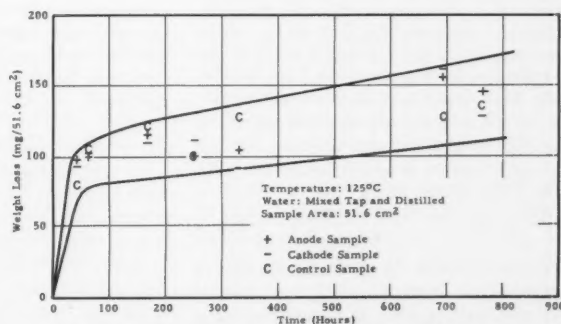
Figure 2—Corrosion of aluminum with 1½-volts applied potential.
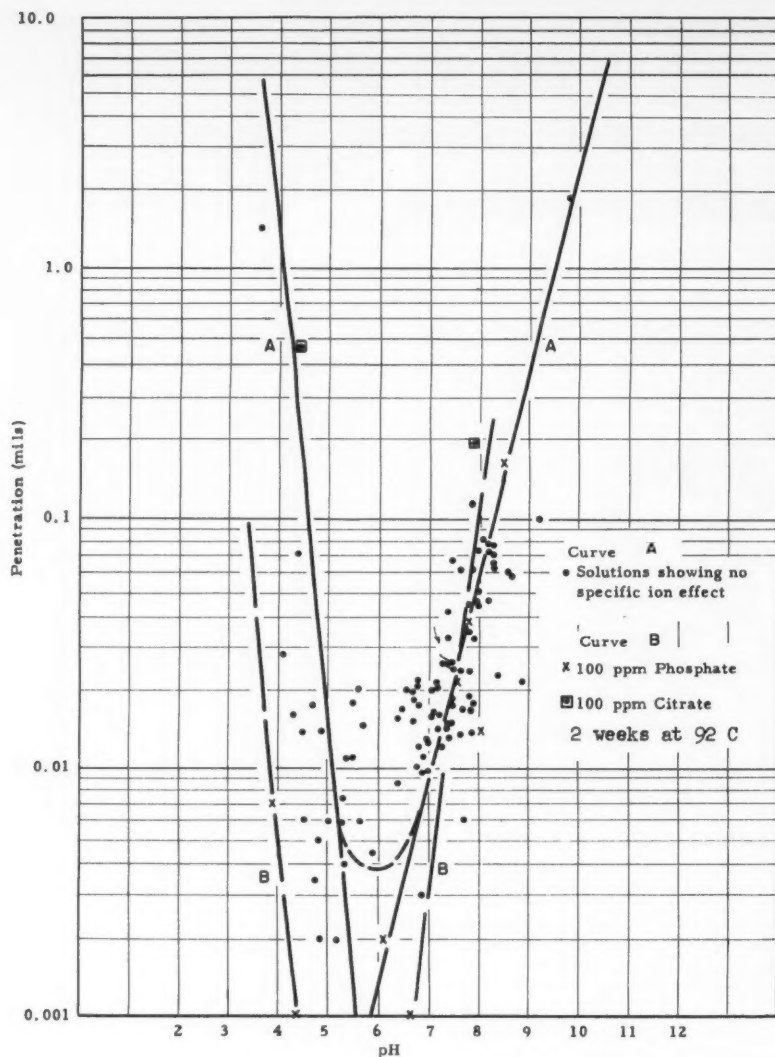
Figure 3—Corrosion as a function of pH.

perature. For example, the maximum barrier voltage in air or water at 300 C is about 2.5 volts which corresponds to a thickness of about 35 A. These findings are in agreement with those of Hunter as quoted by Cohen.[3]

Although the barrier film may comprise most of the corrosion product film formed in dry air, this is not the case in water. For example, at 300 C the bulk corrosion product film formed in water may be several milli-inches thick, but the barrier film is only about 35 A thick. The bulk film consists of a more permeable or porous material which does not affect the barrier film voltage since the barrier voltage remains constant while the bulk film grows in thickness.

The corrosion product films formed in air and water are similar in structure and composition. In their air oxidation experiments, Hunter and Fowle[1] identified the barrier film as amorphous alumina. The corrosion product film formed

on aluminum in water at 300 C was isolated by dissolving the aluminum using the iodine-methanol technique described by Pryor and Keir.[4] X-ray powder diffraction analyses showed that the inner portion of the film consists of amorphous alumina and randomly oriented crystalline Boehmite, $Al_2O_3 \cdot H_2O$. The outer portion, or bulk film, consisted of highly oriented Boehmite. In many other aqueous corrosion experiments over the temperature range of 90 to 350 C, the bulk corrosion product has been identified as Boehmite.

Rate Controlling Process

At temperatures above 100 C the uniform aqueous corrosion of aluminum generally follows a parabolic rate law. Under these conditions the corrosion rate is controlled by the *bulk film* and not the *barrier film*. This conclusion was made from the following considerations and experiments:

1. Three aluminum samples were exposed at 125 C to a mixture of tap water and distilled water having a specific resistance of 25,000 ohm-cm. An external d-c potential of 1.5 volts was applied between two of the samples. The potential drop across the solution was about 0.2 volt. The initial current of several milliamps decreased with exposure time to less than a milliamp. After an exposure of 760 hours, there was no significant difference in the amount of corrosion between the anode, cathode and control as shown in Figure 2. After 760 hours the total weight of aluminum lost was 146 mg from the anode, 128 mg from the cathode and 134 mg from the control. A total of 650 coulombs of electricity had passed between the anode and cathode as indicated by a gas coulometer. This quantity corresponds to 60.5 mg of aluminum as compared to only 18 mg difference in weight loss between the anode and cathode. As seen in Figure 2, there was no consistent relationship between the weight losses of anode, cathode, and control samples run for shorter periods of time. Consequently, although the barrier film thickness is changed by an applied potential, the corrosion rate is not affected.

2. The corrosion rate of aluminum is dependent upon the environment. That is, aluminum corrodes at different rates in air, steam and water of different compositions. The barrier film thickness, however, is independent of the environment.

3. The uniform corrosion rate of aluminum decreases parabolically with time, and the bulk film thickness increases parabolically with time. The barrier film, however, maintains an almost constant thickness. Small variations in barrier film thickness must exist to provide a balance between the transport through the barrier film and conversion to bulk film but these are too small to be observed experimentally.

The bulk Boehmite film can be considered as controlling the corrosion rate. The effective thickness of the bulk film determines the rate at which the environment gets to the barrier film. The environment reacts with the barrier film converting it to bulk film. The replacement of the barrier film is rapid and is *not* a rate controlling process. In a very corrosive environment, a steady state corrosion rate may be reached eventually where a balance exists between the *dissolution* of the *bulk* film, the *conversion* or *barrier* film to *bulk* film, and the *formation* of *barrier* film from the metal. When this steady state is reached, the corrosion rate and the effective film thickness become constant.

Effects of Different Aqueous Environment

Differences in corrosion rates in different aqueous environments appear to be caused by differences in the solubility or composition of the bulk corrosion product film. An extensive series of tests has been completed to determine the effects of various ions on the uniform aqueous corrosion rate of aluminum.[5] Samples were exposed for two weeks at 92 C to solutions made up of various ions and
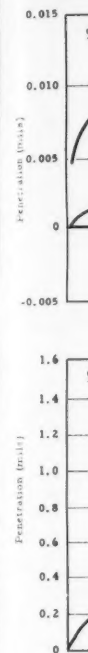
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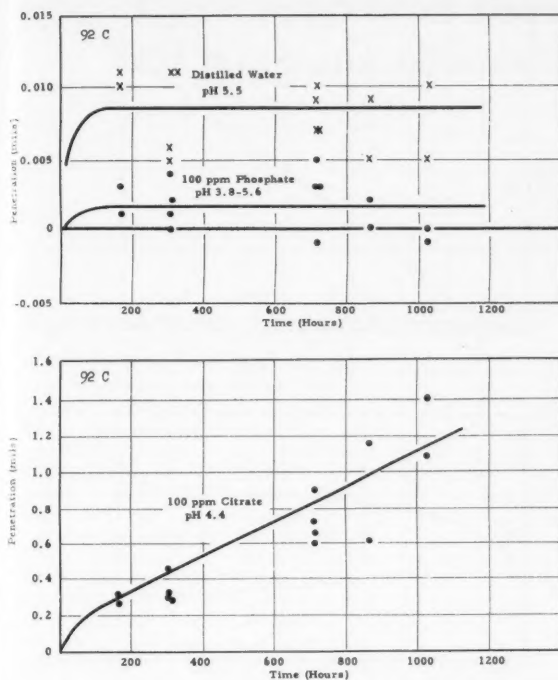
Figure 4—Corrosion as a function of time.

Figure 5—Effect of pH on corrosion product.

combinations of ions in distilled water and reactor process water. The loss in weight of the samples was determined by weighing before exposure and after stripping off the corrosion product film. The pH of the solutions was found to be the most important variable in uniform aqueous corrosion as shown in Figure 3.

The corrosion occurring in tap water, reactor process water, distilled water and distilled water containing up to 100 ppm of chloride, nitrate, sulfate, bicarbonate, hydrogen peroxide, acetate, arsenate, silicate, molybdate and mixtures of these ions is shown in Curve A and was dependent only on the pH of the solution. Solutions of chloride to 10,000 ppm showed no specific ion effect. Of the many solutions tested, only phosphate and citrate ions showed a specific ion effect. Phosphate inhibited corrosion, and citrate enhanced it as shown in Figures 3 and 4.

The inhibiting effect of phosphate ions has been attributed to a modification of the corrosion product film. The film formed at 195 C in a solution of 5 ppm phosphate ions has been identified by X-ray diffraction analysis as augelite, a basic aluminum phosphate, $Al_2PO_4(OH)_3$ or $2Al_2O_3 \cdot P_2O_5 \cdot 3H_2O$. No Boehmite was found. Cohen[3] has reported corrosion products consisting of mixtures of Al_2O_3, $Al_2O_3 \cdot H_2O$ and $2Al_2O_3 \cdot P_2O_5 \cdot 3H_2O$.

The enhancing effect of citrate was attributed to the previously observed complexing of aluminum by citrate,[6] making the corrosion product more soluble and therefore less protective.

The effect of pH on the corrosion product film is shown in Figure 5. Here the ratio of film weight to weight loss has been plotted against pH. Assuming a constant composition of the corrosion product film, this ratio gives a direct measure of the fraction of corroded aluminum remaining in the corrosion product film. The plot is almost identical to Figure 3 where penetration was plotted against pH. This would be expected if the solubility of the corrosion product film was related to the amount of corrosion. That is, a small ratio indicates a high solubility of the film and a more severe corrosion. A maximum ratio indicates a minimum solubility and, consequently, a minimum corrosion. If the corrosion is determined by the solubility of the oxide film, the presence of dissolved aluminum ions could inhibit corrosion by a common ion effect. This effect has been observed.

The lower corrosion rates observed in static systems, as compared with dynamic systems, are considered to be caused by a build up in concentration of dissolved aluminum ions. Increasing the aluminum surface to environment volume ratio in dynamic systems increases the aluminum ion concentration and decreases corrosion rates. Recently it was observed that corrosion is inhibited by aluminate ions in a basic solution.[5]

Intergranular Penetration Corrosion

The role that the oxide film plays with regard to the intergranular penetration corrosion is considered here. In high temperature water or steam, at about
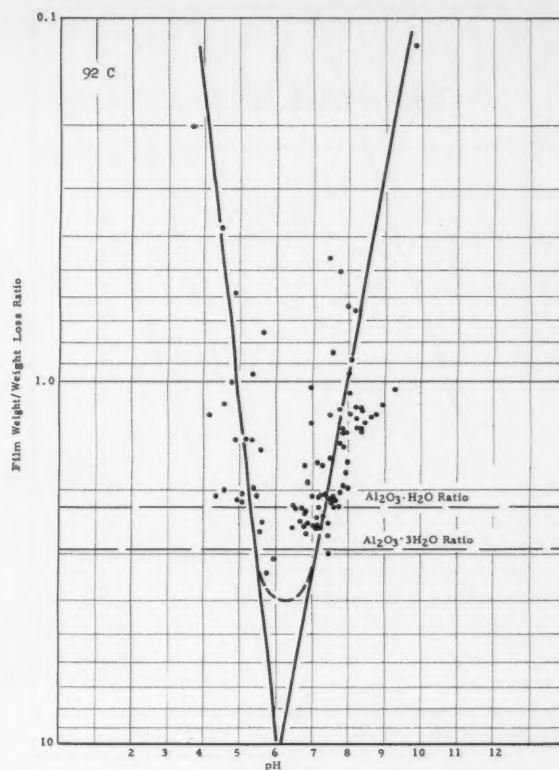
250 C and higher, aluminum corrodes uniformly for a period of time which decreases with increasing temperature. After this period of time, intergranular penetration corrosion begins and the corrosion rate is dramatically increased. Figure 6 shows the variation of this induction time with temperature. High temperature air oxidation studies of Hunter and Fowle[1] showed that the amorphous barrier film becomes crystalline η alumina after a period which decreases with increasing temperature. This change has been observed at temperatures of 370 C and above.

The similarity between the induction time for crystallization of the barrier film in air and the induction time for intergranular corrosion in water or steam is intriguing. It seems possible that they are the same type of phenomenon and that the intergranular corrosion of aluminum is caused by or is accompanied by a crystallization process in the barrier film. There is some evidence for this. X-ray diffraction analysis of the inner surface of the corrosion product from a sample of intergranularly corroded aluminum showed the presence of η alumina and the absence of the amorphous material. Also, experiments were performed in which the barrier potential was measured on samples of aluminum exposed to water at about 350 C. The results are shown in Figure 7. The barrier film grew rapidly at first, but after a short period the barrier film broke down, and at the same time intergranular corrosion of the aluminum began.
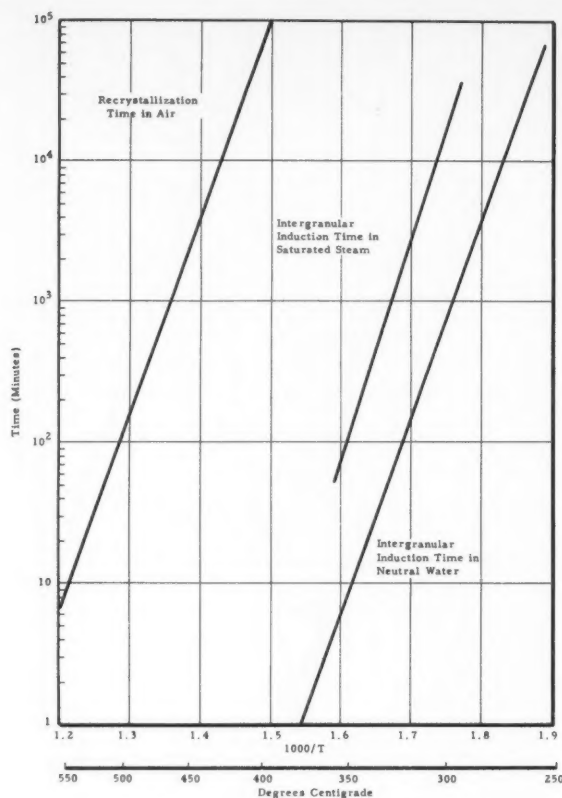
Figure 6—Recrystallization time and intergranular induction time for 1245 alloy.

Figure 7—Barrier voltage and weight gain as a function of time.

Some conclusions on the effect of alloying can be drawn. In most cases different aluminum alloys do not differ in their uniform corrosion rates, but they do differ in their induction times and rates of intergranular attack. The intergranular attack proceeds at a constant rate in spite of the increasing thickness of the corrosion product film. Therefore, the bulk film must not control the rate of intergranular attack. From these observations, it can be inferred that the effect of alloying is manifested in the base metal and/or barrier film and not in the bulk corrosion product.

Conclusions

The following conclusions have been reached concerning the role of the corro-sion product film in the aqueous corro-sion of aluminum:

1. The corrosion product film formed on aluminum in water consists of a thin compact barrier film adjacent to the metal and a thicker, more permeable bulk film.

2. The barrier film is amorphous, and the bulk film consists of a crystalline hydrated oxide.

3. The uniform corrosion process is controlled by the bulk film, not by the barrier film.

4. The composition of the water affects the corrosion rate by altering the solu-bility and composition of the bulk film.

5. The onset of intergranular attack is

caused possibly by or accompanied by crystallization of the barrier film.

6. The bulk film does not control the rate of intergranular attack.

7. The effect of alloying is manifested in the base metal and/or barrier film, but not in the bulk film.

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Any discussions of this article not published above will appear in the June, 1959 issue

Observations on the Mechanisms and Kinetics Of Aqueous Aluminum Corrosion

By R. L. DILLON

Introduction

CONSIDERABLE INTEREST in aluminum for use in high temperature water cooled reactors has been shown in recent years. Laboratories in this country, Canada and Europe are examining the corrosion resistance of aluminum alloys under reactor conditions. Emphasis has been on the development of resistant alloys and establishment of approximate corrosion rates, sufficient for alloy comparison and preliminary reactor design purposes. This report presents some of the Hanford corrosion data, which have been analyzed in detail and appear adequate to permit some speculation about the mechanism of the corrosion process. This report also examines the relationship between the oxidation process in air and water. The rate laws associated with water and air oxidation and the kinetic constants derivable from the rates will be considered and compared.

Oxidation of aluminum in dry air and oxygen is better understood than water oxidation. Air oxidation has been described and analyzed by several investigators over a wide temperature range. To the extent that air and water systems seem analogous, the more extensive literature on air oxidation will be used to help establish a tentative mechanism for the water oxidation process.

Experiments

A recent series of long-term corrosion tests of aluminum have been conducted in static and low flow deionized water. These tests included 24 alloys which, in the course of a previous survey and on the basis of off-site experience, appeared to have good resistance to intergranular attack in high temperature water.[1] The alloys were tested at various temperatures from 100 to 363 C for periods of ten minutes to one year. The tests were conducted in five-liter autoclaves, each equipped with a pump, flow control valve, etc., required to maintain a 1-gph flow of deionized water through the system. Essential features of the train are shown in Figure 1. The material in contact with the water was 300 series stainless steel throughout.

Samples were withdrawn in duplicate with about eight withdrawals per run. In M-388 alloy no significant corrosion differences were noted between annealed

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and as-rolled samples. Average penetration in mils (0.001 inch) was calculated from metal loss. Lacking an effective film stripping procedure, corrosion product was isolated by dissolution of unoxidized metal in methanol-iodine solution.[2] Weight loss was calculated from weight of corrosion product and weight of sample before and after exposure.

Results

The main conclusions from these tests are the following:

1. For the more resistant alloys under experimental conditions, the corrosion process has a parabolic dependence on

Abstract

The corrosion of Al in high temperature deionized water in the range 100 to 363 C has been studied as a kinetic process. The observations described in the report coupled with lower temperature data taken from the literature indicate aluminum corrosion successively has a logarithmic, a parabolic and a linear dependence on time as the temperature increases. The temperature dependence for parabolic and linear processes have been determined. Certain similarities between air and water oxidation are pointed out and discussed. The effect of alloying additions has been considered and found to be negligible for the parabolic process, but important in the linear oxidation process.

3.8.4

time, though departures from this law are observed after long exposures at the higher temperatures. The parabolic dependence of corrosion on time, $Corr = K_r t^{1/2}$, can be demonstrated by a plot of logarithm of corrosion against logarithm of time. In Figure 2, log corrosion at 350 C has been plotted against log time from which a slope of 0.51 ± 0.026, within 95 percent confidence limits, was determined by a least squares technique. This is not significantly different from a slope of $1/2$ required by a parabolic corrosion process. Figure 3 shows some corrosion data for the alloy M-388 at various temperatures plotted on parabolic axes. Logarithms of parabolic corrosion constants for M-388 alloy in deionized water are plotted against reciprocal temperature in Figure 4. From this plot, activation energy and entropy of activation are calculated by the Gulbransen method which is specific to diffusion controlled
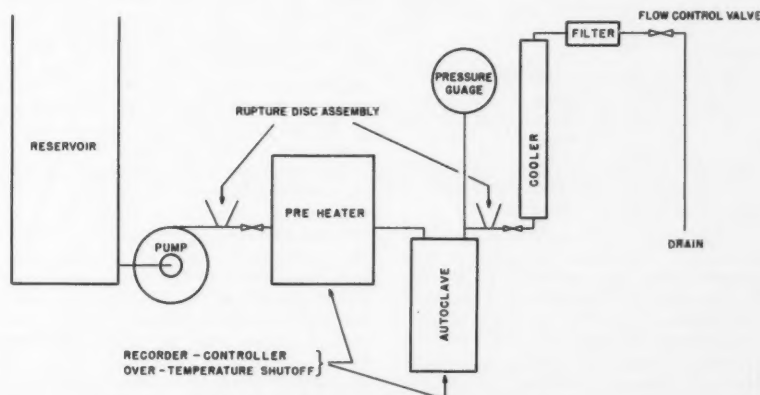
Figure 1—Schematic diagram for flowing autoclave.
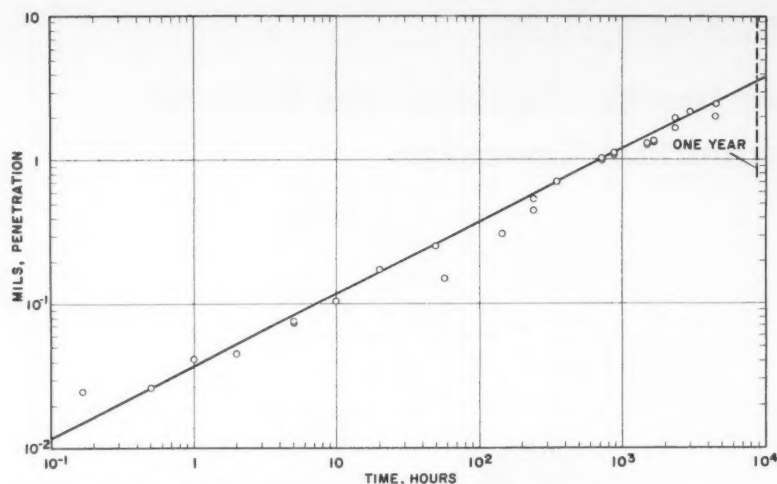
Figure 2—Corrosion of M-388 aluminum alloy in 350 C refreshed deionized water. Evaluated by least squares method as 0.51, the slope establishes parabolic character of the corrosion process.

TABLE 1—Parabolic Rate Constants for Aluminum Alloys in 350 C Refreshed Water*

Alloy	Major Constituents, %	Rate Constant mils/yr$^{1/2}$
172961	11.2 Cu, 0.31 Mn, 0.1V, 0.17 Zr	3.1
173160	6.1 Cu, 0.31 Mn, 0.18 V, 0.23 Zr	3.0
173162	6.0 Cu, 0.76 Fe, 0.30 Mn, 0.25 Ni, 0.9 V, 0.14 Zr	2.8
173166	3.0 Cu, 0.61 Fe, 6.97 Si, 0.16 Mg, 2.94 Ni	3.5
173212	7.8 Cu, 0.74 Fe, 0.31 Mn, 0.28 Ni, 0.10 V, 0.12 Zr	3.2
X2219	6.2 Cu, 0.19 Fe, 0.11 Si, 0.32 Mn, 0.12 V, 0.16 Zr	3.7
M388	0.48 Fe, 1.02 Ni	3.5
M400	0.86 Fe, 1.3 Ni	3.7
2018	4.0 Cu, 0.6 Mg, 2.0 Ni	3.3
4032	0.9 Cu, 12.2 Si, 1.1 Mg. 0.9 Ni	3.4

* The similarity in rates for alloys of widely differing composition could equally well have been demonstrated at other test temperatures.

TABLE 2—Derived Kinetic Constants for Oxidation of Aluminum

Oxidation Rate Law	Air-Oxygen [4, 9]		Temp. Range	Water		Temp. Range
	ΔH*Kcal	ΔS*e.u.		ΔH*Kcal	ΔS*e.u.	
Inverse logarithmic			200C			100C
Parabolic	21.4	—28.6	350-450	12.2	—24	100-350
Linear	47.7		400-550	47		350

* The substantial differences in rate for air and water oxidation may be related to differences in diffusing species or extent of defect structure in the oxide.

parabolic rate processes.[3] The Gulbransen equation has the form

$$K_r = \frac{2kt}{h} \lambda^2 \exp \Delta S^*/R \exp —\Delta H^*/RT$$

where

  k = Boltzmann's constant
  h = Planck's constant
  λ = interatomic distance in the oxide, 2.74 Å for Al

The value of the activation energy has been calculated to be 12.2 Kcal; the entropy of activation, —24 e. u.

2. The rate of the parabolic corrosion process is a function of temperature and perhaps other environmental factors, being essentially independent of the alloy composition. Table 1 is a compilation of several high temperature alloys showing composition and the value of the parabolic rate constant evaluated graphically at 350 C.

3. For all alloys at sufficiently high temperatures, the parabolic corrosion process was followed by a more rapid linear rate process. For the most resistant alloy, M-400, the transition was found to take place after two months at 363 C. The transition for the other alloys was observable at 350 C from two to six months. The increase in rate of corrosion of M-388 resulting from the change in kinetics is shown in Figure 5.

For the linear water oxidation process, an activation energy for the alloy M-388 has been evaluated over a necessarily restricted temperature range, 350 to 363 C. At temperatures below 350 C, the induction time prior to the initiation of the linear process is too long to be readily measured; an upper limit, 374.4 C, is the critical temperature of water. The activation energy evaluated from data at 350 and 363 C is 47 Kcal which agrees with values for other alloys in water.

Discussion

Comparison of Rate Laws for Air and Water Oxidation of Aluminum

In dry air or oxygen a transition from parabolic to linear dependence on time occurs which is similar to that described above for water oxidation. In temperatures from 300 to 450 C, air oxidation has a parabolic dependence on time. From 450 to 600 C, air oxidation is a linear process.[4]

At temperatures below 300 C, Mott[5] and Cabrera[6] showed on theoretical grounds that air oxidation of aluminum should follow an inverse logarithmic dependence on time. Inverse logarithmic time dependence for aluminum air oxidation has been verified experimentally by refined electrochemical techniques.[7]

At 100 C, the lowest temperature used in these corrosion data, the oxidation process was parabolic. However, data of Draley and Ruther at 50 C show a qualitative similarity to low temperature air oxidation of aluminum.[8] Figure 6 shows the relatively rapid corrosion in the initial minutes of exposure, after which corrosion virtually ceases. The three kinetic regimes observed in air oxidation probably occur in the water process also.

Comparison of Energies and Entropies of Activation

While aluminum oxidation rates are much greater in water than air or oxygen (a factor of 100 at 350 C[(1)]) examination of pseudo-thermodynamic constants derived from rate constants for air and water phase corrosion provides another basis for comparing the processes. Table 2 is a comparison of kinetic constants from air[4] and water oxidation.

According to W. J. Moore in a discussion of the parabolic oxidation processes of a variety of metals, the unusual feature of aluminum air oxidation is the low activation energy and the large negative entropy of activation.[9] Both of these features are observed in the water oxidation process also. For the linear process, according to Moore, a high activation energy and relatively large frequency factor (not listed here) are the characteristics of aluminum corrosion. In water oxidation, a large activation energy is found. While the frequency factor has not been evaluated, it is even larger than in the air process.

Further Comparisons

A further element of similarity between air and water formed corrosion product has been demonstrated by V. H. Troutner[10] in the previous paper. He has applied the method of Hunter and Fowle[11] for determining barrier layer thickness of air formed films to aqueous corrosion product. Summarizing the investigation of both air and water formed oxides, the voltage required to pass an appreciable current, the so-called anodizing voltage, is a function only of the temperature at which oxidation of the sample took place. That is, the electrical properties of the

(1) The substantial differences in rate for air and water oxidation may be related to differences in diffusing species or extent of defect structure in the oxide.
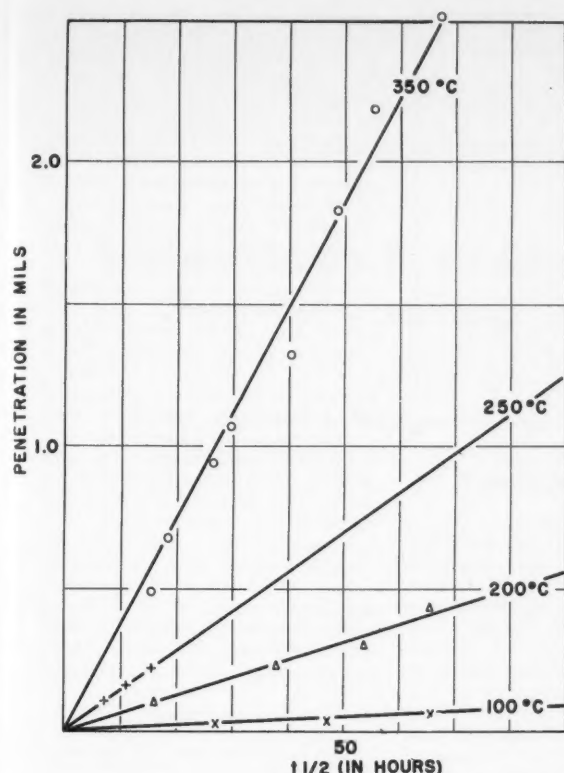
Figure 3—Corrosion of M-388 alloy in low flow deionized water, plotted as a parabolic function of time.
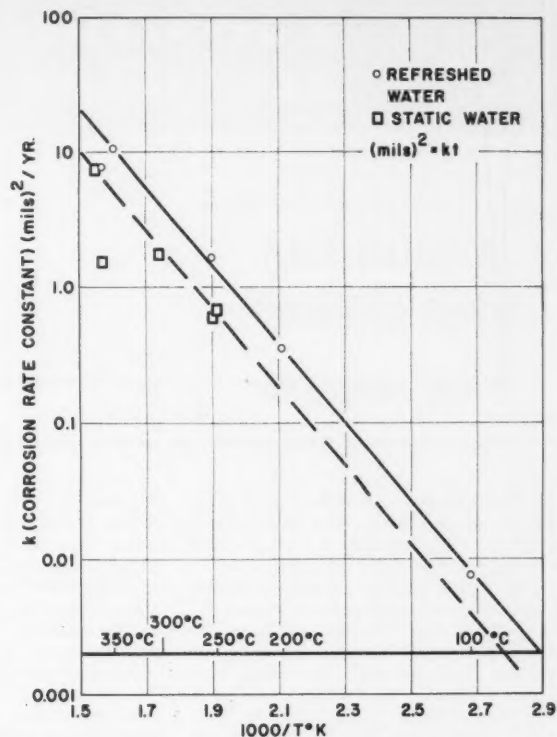
Figure 4—Dependence of the parabolic rate constant on temperature for the corrosion of aluminum in water.

Figure 5—Corrosion of M-388 alloy in 363 C static deionized water showing transition from parabolic to linear dependence on time. Each point is the average of two or more determinations.

oxide film are essentially independent of time at temperature and independent of environment whether water or air.

Interpretation of Kinetic Data in Terms of an Oxidation Mechanism

From the observations cited above, a qualitative picture of the aqueous corrosion process can be formed. In low temperature water as in low temperature air, the environment is relatively non-corrosive. A layer of protective oxide is formed rapidly, and the reaction rate diminishes to a very low value. Generally, growth of the barrier film proceeds by diffusion of metal ions through the N-type oxide (excess metal ions).

The parabolic rate process observed for both air and aqueous oxidation at intermediate temperatures requires at least a duplex corrosion product. From barrier film measurements, using the anodizing technique described in the preceding paragraph, the presence of a thin film of constant thickness can be established. However, since the oxidation rate is dependent on time (and thickness of the total film), the rate determining process must depend on the extent of the bulk film.[2] The transport process per unit thickness of oxide is more rapid through bulk film than through barrier film. However, because of the greater thickness of the bulk oxide, transport through it is the rate determining step.

Whether the diffusing species are metal ions, oxygen (or hydroxyl) ions or oxygen atoms is a problem that needs to be answered. There is some reason for believing that it is hydroxyl or oxygen ions that migrate through the bulk oxide. It can be argued that, if hydroxyl (or oxy-

gen) ion diffusion did occur at grain boundaries during oxidation, it could account for the low activation energy and large negative entropy of activation.[9, 12, 13] Diffusion of hydroxyl ions to the barrier-bulk oxide interface also would provide a mechanism for conversion of the bar-

(2) From kinetics alone, it is not possible to distinguish between a dependence of rate on thickness of bulk film and of a conjectural oxide layer whose thickness is approximately proportional to the total bulk oxide.
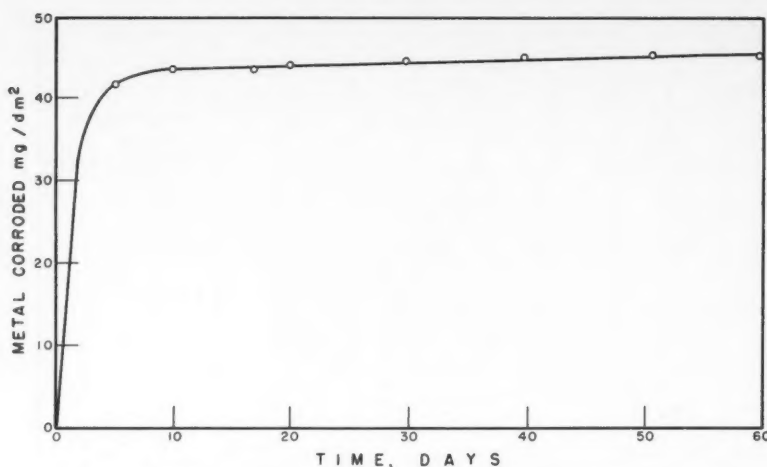
Figure 6—Corrosion of 2S aluminum in oxygen saturated water at 50 C (from ANL-5001).

rier film material (amorphous and anhydrous) to the bulk film composition which is crystalline and, at least in water environment, partially hydrated.

The nature of the changes occurring within the bulk oxide which convert the rate process from parabolic to linear are not understood. Since the corrosion rate remains constant while the oxide continues to grow in thickness, diffusion through the oxide is no longer the rate determining factor. The presence of certain alloying agents alone or in combination apparently extend the time and temperature range in which the bulk film is protective and rate determining. Gulbransen and Wysong have discussed the transition from parabolic to linear time dependence for air oxidation of aluminum.[4] They observed linear rates, that is, rates independent of film thickness for aluminum oxidation at 500 C even for thin films, 100 Å. They rejected mechanical failure of the film as the cause of linear rates. They contend that thin films are unlikely to develop stresses sufficient to cause cracking with resulting admission of oxygen to the metal surface. Instead, they assume a rapid new ion transport process which comes into play at high temperatures. The rate determining

step becomes the rate of ion formation. Water formed films are thick enough to allow consideration of film cracking. However, the similarity of the temperature dependence in water to the linear process occurring in air suggests the cause of the transition may be the same in air and water.

From the rate data and the mechanism for aluminum corrosion suggested here, some predictions about the behavior of aluminum in high temperature water can be made. In deionized water at temperatures from 100 to 350 C, aluminum corrodes by a parabolic process; the corrosion rate is inversely proportional to the thickness of the corrosion product. Any experimental conditions which remove oxide by erosion or render it porous by dissolution will increase corrosion rates over those experienced in autoclaves with low water throughput. It has been observed experimentally in dynamic test facilities at Hanford that, as deionized water is equilibrated with aluminum oxide at test temperature, it becomes less corrosive.

Table 1 shows that the effect of alloying additions in the more promising alloys described here has been to raise the temperature at which the transition from

parabolic to linear process takes place. For alloys of widely varied chemical composition, the parabolic corrosion rates at a given temperature are alike. For significant improvements over such alloys as M-388 and M-400, alloys must be devised which corrode even at high temperatures by the logarithmic rate processes typical of aluminum in low temperature moist air and probably water. The temperature must be raised at which the transition from logarithmic to parabolic rate processes take place in the same way which current alloys have raised the transition from parabolic to linear. The corrosion process for such an alloy would involve rapid initial corrosion after which corrosion would greatly diminish. Preliminary investigations of a class of alloys, which apparently have these corrosion characteristics, are being made.

Corrosion behavior appears to be closely related to the nature and thickness of the oxide film. Current knowledge of the chemical and structural nature of water-formed aluminum corrosion product is meager. Study of the oxide would extend present knowledge of the corrosion process, particularly the effect of alloying additions present in the metal. Studies are also needed to identify states of the oxide corresponding to various kinetic behaviors.

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**Any discussions of this article not published above
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Precautionary Procedures In Chemical Cleaning*

A Contribution to the Work
Of NACE Technical Unit Committee T-8A
On Chemical Cleaning,[1] By Robert A. Stander[2]

Introduction

WITH THE development of highly effective acid inhibitors, increased emphasis has been placed on the chemical removal of scales and sludges deposited in process and other equipment. Along with this increase in the utility of chemical cleaning, other factors affecting its efficiency, corrosion control and safety have come to light. It is the purpose of this paper to outline the important safety precautions which should be taken under varying conditions.

In the following discussion it will be shown why it is necessary for the customer to exercise control of and to participate in the cleaning operation. Such matters as corrosion allowance, types of scale, previous history of the use of equipment, disposal of waste, testing of corrosion rate, etc., can be determined only by the customer. Furthermore, it is felt that chemical cleaning work should be handled by a reputable cleaning company on a term contract basis rather than on an individual job basis. With the amount of testing and planning which is necessary for a good operation, equipment would be out of service too long if additional time were required to review bids each time. The cleaning company can do better and faster work as they gain knowledge of the specific plant equipment and personnel. The dangers of always doing business on a low bid basis without regard to control will be brought out later in this paper.

Precautionary Procedures

The two most important phases of chemical cleaning are: (1) The acid removal of water scales, mill scale and products of corrosion, and (2) The

emulsifying or solvent removal of process deposits that are not soluble in an inorganic acid.

It is the acid cleaning that requires the most attention with respect to corrosion control in cleaning. Hydrochloric acid in concentrations ranging from 3 percent to 15 percent is the most commonly used solvent for water scales, mill scale and corrosion deposits. Acid etching or corrosion of equipment is prevented, or reduced, by the addition of an acid inhibitor. A great number of inhibitors of this type are on the market. However, not all of these inhibitors are effective for concentrations and temperatures used in chemical cleaning.

Proper types and concentrations of inhibitors must be ascertained for each set of conditions. This can be done by coupon corrosion tests of the metal in question, submerged in an inhibited acid solution strong and hot enough to dissolve the particular scale in a certain number of hours.

Allowable rates of acid corrosion will depend upon the frequency of cleaning and the total corrosion allowance. Certain types of equipment might require acid washing only once or twice during their entire operating life while other types might need cleaning as often as every few weeks. These examples, of course, represent extreme cases.

On a high pressure steam generating boiler, for instance, a chemical cleaning might be in order every six months. On this basis a maximum allowable corrosion can be set up in terms of mg/sq cm/hr, lbs/sq ft/day, mils/hr, etc. In the boiler case just cited, several customers worked out a maximum corrosion rate of about 0.8 mg/sq cm/hr (0.04 mils/hr) based on a six hour treatment every six months.

Regular repeat maintenance removal of boiler scales, predominately carbonates, will require a cleaning solution of about 4 percent HCl at 160 F. This solution strength and temperature is relatively easy to inhibit. As a matter of

Abstract

Safety procedures to be followed in chemical cleaning of equipment are outlined. Topics discussed include inhibition of cleaning acid by test before new jobs, control of temperature and concentration during cleaning operation, providing of adequate facilities for flushing following the acid stage, use of fresh acid to replace "poisoned" acid, elimination of conditions promoting galvanic corrosion, and removal of poisonous gases. The need for closer coordination between the cleaning contractor and the customer is brought out in this report. 5.9.2

fact, one inhibitor on the open market, when used at a rate of 0.5 percent based on the concentrated degree Baumé muriatic acid, produced a corrosion rate of only about 0.07 mg/sq cm/hr (0.0035 mils/hr) at 160 F when diluted to 4 percent. This is under the maximum permissible rate by a factor of more than ten.

In testing inhibitors it is important to get an average corrosion rate for the entire proposed treating period. Many inhibitors look good for the first hour or two, but at elevated temperatures tend to break down with time.

Testing also should be done in the presence of the scale to be removed, because the reaction products often will either add a new corrosive element or will have the effect of "poisoning" the inhibitor. Such a "poisoning" effect may result from a cleaning operation in which iron sulfide is present in the scale. Hydrogen sulfide liberated during the reaction reduces the efficiency of most acid inhibitors, which stand up excellently in the absence of hydrogen sulfide. As an example, one corrosion control test run with 10 percent inhibited hydrochloric acid at 177 F for two hours showed the following weight losses on polished carbon steel coupons:

Sample A—Nothing added to inhibited acid: 0.5 mg/sq cm/hr, or 0.025 mils/hr.

Sample B—H_2S bubbled through acid during test: 13.0 mg/sq cm/hr, or 0.65 mils/hr.

Another situation that often develops is the ferric ion corrosion problem. This is generally recognized, but not often considered during chemical cleaning. The buildup of ferric chloride in solution while dissolving iron salts with HCl must be prevented, and the only practical way to do this is by the introduction of ample fresh acid. There probably will be sufficient acid present in the system to completely dissolve the scales present but all the same, fresh acid must be introduced to maintain ferric ion concentration below the critical level. Alquist[1] presents a detailed discussion of the principles of this type of corrosion, and states, "The reaction, $2FeCl_3 + Fe = 3FeCl_2$, is shown to be true by the increase in corrosion of steel in inhibited acid when ferric ions are present. The acid corrosion inhibitor which protects the metal from attack by acid has no restraining effect on the corrosion of the metal by the ferric ions."

This particular reaction product oxidizing agent is certainly the most common, but it is by no means the only, or the most corrosive such agent. Another commonly encountered oxidizing agent is the cupric ion, frequently brought into solution in boiler cleaning where metallic copper has been picked up in the condensing or preheating sections, and laid down as a thin sheet on the boiler tubes. Copper removal warrants a discussion in itself, but attention will be called here only to the corrosiveness of the cupric ion in solution. It can be seen that corrosion control methods developed in the laboratory must take into consideration not only the solvent, but also the reaction products. The addition of fresh inhibited acid is the only practical way to prevent this type of corrosion. In no case where this type of reaction product develops is it permissible to use partially spent acid from one cleaning operation in another piece of equipment.

This last statement is one which must be insisted upon by the customer, (particularly in cases where purchasing practices permit acceptance only of the lowest bid). Acid cleaning quotations are usually based on cost of cleaning agent and time required to carry out cleaning operations. The use of partially spent acid allows a contractor to submit a lower bid than in cases where fresh acid is used.

Cast iron systems, such as tower trays and bubble caps, compressor engine water jackets, etc., require an entirely new set of laboratory corrosion data. It is actually possible to boil 3 percent to 5 percent HCl with live steam in towers with no serious graphitization or etching if the proper additives are employed. Even aluminum may be treated with HCl.

A very serious corrosion problem involved in the use of these highly ionized solvents is, of course, the galvanic or cellular one. Many times serious galvanic action between two dissimilar metals has been blamed on acid cleaning. In systems where more than one type of metal

is present, care should be taken to insulate the metal juncture, or preferably the less common metal should be removed. For short treating periods in certain cases this cellular corrosion may not bear any weight, but it still should be considered before every cleaning job.

An all stainless steel system can be cleaned effectively with sulfuric or nitric acid. However, if any portion of the material has operated at sensitizing temperatures for any period of time, and this includes the stabilized grades, it is extremely unlikely that any acid cleaning could be performed without intergranular attack.

Toxic Hazards

Precautionary procedures must be undertaken to prevent toxic hazards which may occur during chemical cleaning operations. These hazards sometimes include exposure to the cleaning agent itself. In such cases normal safety practices must be adhered to, and proper protective clothing must be worn.

More often hazards in chemical cleaning arise from chemical reaction between the solvent being used and the material being removed, and between the solvent and the metal of which the equipment is made. Toxic gases caused by such reactions are fairly common, and must be anticipated in kind and quantity, and the proper safety precautions made. Venting control must be complete to dispose of the evolved gases to a flare stack or other disposal point or through some absorbing solution. Since these poisonous gases are hydrides, attention will be directed primarily to acid cleaning solutions. Weak acids (sometimes even water) will evolve hydrides from many of the salts of sulfur, phosphorous, arsenic, antimony, tin, and other metals occurring as traces, and cyanide. Also the solution of nascent hydrogen (formed by acid attack on iron, steel, copper, etc., or by caustic attack on aluminum and zinc), in its highly active form will evolve hydrides from the above salts.

The hydride of sulfur (H_2S) is probably the most frequently evolved gas. When inhaled, this gas prevents the human body from utilizing oxygen. Its very disagreeable odor, not present with some of the other gases, is in itself a safety factor. Safety precautions adequate for H_2S will help for some of the other gases, but it should be remembered that the hydride of arsenic, arsine, for instance, is very dangerous in concentrations of 1 ppm over several hours. Arsine destroys red blood cells and attacks the liver. Hydrogen sulfide, on the other hand, becomes dangerous in concentrations of 150 ppm or more, over a period of several hours.

Blue iron cyanides will evolve HCN in the presence of HCl. They are found most commonly as deposits in the recovery sections of fluid catalytic cracking units. Hydrogen cyanide acts in a similar manner on humans as H_2S, but is toxic in concentrations of about half

that of hydrogen sulfide. It may also be absorbed, like its soluble salts, through the eyes and skin. Arsenic itself occurs in many ways. It was used very widely several years ago as an acid inhibitor, before more effective organic inhibitors were developed. It occurs in small quantities in several alloys, notably admiralty brass, and may also be present in refinery feed. Other gases, such as hydrogen phosphide, hydrogen arsenide, etc., are all to be considered, but their occurrence is rare, and as such are beyond the scope of this paper. Proper disposal of hydrogen sulfide, hydrogen cyanide, and hydrogen arsenide, will cover all cases in the experience of the writer.

It is of prime importance that the chemical cleaning contractor and the customer discuss the types of deposits and metals present, and the type of solvent to be used, prior to the carrying out of the cleaning operation. If this is not done, unsuspected toxic gases could cause grave damage or even death. There have been several instances of death in the history of chemical cleaning, which could have been avoided if a more thorough study of the cleaning operations had been made before cleaning was begun.

Conclusions

A meeting between cleaning contractor and customer will result in benefits in addition to increased safety of operations. If precleaning equipment inspection, scale and sludge solubility tests, and the resulting determination of cleaning conditions are made, the following benefits can result:

1. The cost estimate will be based on contractor's and customer's specifications, and will include sufficient time and material to eliminate many corrosion possibilities.

2. The work itself will be performed with greater probability of maximum safety and efficiency.

3. The customer will know the condition of his equipment before cleaning, and with after-inspection, will be able to determine the benefits of chemical cleaning and the results to anticipate in the future.

4. New cleaning techniques are more likely to be developed with the combination of research resources.

5. Cleaning itself is a joint responsibility. In many cases cleaning jobs prove unsatisfactory because of a lack of advance information, and cooperation. In the last ten years, secrecy regarding chemical cleaning techniques has practically disappeared.

The following precautionary procedures should be observed on every chemical cleaning job:

1. Proper inhibition of the cleaning acid by test before each new job, considering concentration, temperature and time of treatment, metals involved, and

reaction products from the acid and scale of metal.

2. Careful control of temperature and concentration during the cleaning operation itself.

3. Adequate facilities for complete flushing and/or neutralization following the acid stage.

4. Sufficient supply of fresh acid to replace that which has been "poisoned" by hydrogen sulfide, ferric ion, etc.

5. Elimination, wherever possible, of conditions whereby galvanic action may be accelerated. For instance, stainless steel gaskets and valves in a low-carbon steel system should be replaced for the cleaning cycle.

6. Proper provisions for the removal, by venting or absorption, of gases, both poisonous and explosive, such as hydrogen. If evolved gases in general are properly disposed of on every job, no problem need ever arise.

It has not been the intent or within the scope of this discussion to present detailed information regarding corrosion rates under various conditions, nor even each specific condition under which corrosion might occur. The objective has been to outline the more common hazards encountered in chemical cleaning, and to point out the absolute necessity for following a few important precautionary procedures. Above all, chemical cleaning should not be considered in a

routine manner. There are new specific hazards encountered in each operation.

Further research is specifically needed for:

1. The development of unsuspected conditions leading to corrosion in chemical cleaning, and the proper procedure or inhibitor to be used for each such condition.

2. Detailed information regarding galvanic or electrolytic and crevice corrosion which may occur during or be caused by chemical cleaning.

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Aluminum Cooling Towers and Their Treatment*

By A. J. HAYGOOD and J. DEAN MINFORD

Introduction

GENERAL WATER shortage, caused by receding water tables and increasing demands, is forcing many municipalities to put restrictions on the use of water. Water used for various cooling processes constitutes a large portion of the demand. Once-through cooling systems in many areas now are prohibited because of the potential over-loading of sewers and sewerage treatment facilities. Cooling towers are being used as one effective means of coping with both these situations.

Aluminum alloys with their characteristics of light weight, good resistance to corrosion and low fabricating and maintenance costs have been employed as materials of construction for cooling towers.

Considerable data on the performance of aluminum alloys when exposed to various waters have been acquired through research. This knowledge is being broadened by periodic examination of several aluminum towers now in service and of test racks exposed in typical operating towers throughout the United States. Research laboratories operate experimental towers where water conditions can be varied, different alloys evaluated and comparative performances determined for alternate types of construction. Recommendations are made on alloy selection, fabricating practice, surface finish and water treatment.

Corrosion engineers agree on the desirability of eliminating dissimilar materials in systems handling recirculated waters. While this can seldom be achieved throughout the entire water circuit, undesirable combinations of metals can be avoided in the tower itself. Attention paid to details during design and fabrication of the tower can minimize maintenance costs.

Parts fabricated of copper, its alloys and other heavy metals such as nickel and lead should be avoided in an aluminum tower. Since zinc is anodic to aluminum in most waters, these two metals can be used in contact. Stainless steels of the 300 series generally are compatible with aluminum alloys if relatively small surface areas of the steels are exposed.

Alloy Selection

Designers may choose from a large selection of aluminum alloys. Even the small builder should exercise care in selecting from warehouse materials since he may pay a premium for high strength or other characteristics not required. The strain hardenable alloys and medium strength, heat treatable alloys generally

Haygood   **Minford**

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Abstract

Characteristics of aluminum alloys are discussed to show the use of this material in cooling tower construction. Alloy selection, fabricating practice, surface finish and water treatment are covered. Examples of cooling tower installations and data from field research are given.   7.4.1

are used since they offer the best combination of strength, formability, resistance to corrosion and low cost. Outstanding in resistance to corrosion, alclad products are designed to provide high resistance to perforation. The core of alclad products is selected for the structural or formability requirements of the design; the cladding is selected to afford cathodic protection to the core. The alclad layer may be present on one or both surfaces of a sheet or on the walls of tube. The cladding composition and thickness vary with alloy and product. Figure 1 shows the character of attack on an alclad surface as compared to that of a non-clad surface. The cladding is anodic to the core alloy and electrochemically protects it from corrosion, thus limiting the depth of penetration to the thickness of the alclad coating. Alclad aluminum products have been used successfully for many years in applications ranging from the everyday teakettle and steam iron to underwater pipelines and surface condensers in power plants.

In cooling towers, alclad alloys are recommended for the basin and side sheets because the recirculated water may contain dissolved salts of heavy metals picked up in the system. Alclad materials should

be used for drip eliminators, fan cowlings and roof decks. Alclad 3003 or Alclad 3004 in the annealed —H12 or —H32 temper could be used for these parts, depending on the formability and strength required. The thickness allowance for corrosion which is often made in selecting steel sheet gauges may be reduced in designing an aluminum tower because of aluminum's resistance to corrosion. A minimum gauge of 0.064 inches for siding and 0.090 inches for basin sheets is suggested for the above alloys, depending upon strength considerations.

The following list of components of a typical tower includes the recommended aluminum alloys:

Structurals: 6061-T6, 6062-T6 and 6063-T6.

Fan blades: forged, 6051-T6; stamped sheet, 5052-H32; cast, 356-T6.

Decking or fill formed of sheet: Alclad 3004-H14 (minimum gauge 0.032 inches).

Bolts: 2024-T4 with No. 205 Alumilite Finish or 6061-T6.

Nails: 6061-T91.

Rivets: 6053-T61.

Screw machine parts: 6061-T6.

Castings: 43 or 356-T6.

All piping inside the tower, such as distribution and spray headers and overflow standpipes, should be of Alclad (inside) 3003 pipe. The cooled water outlet, which will probably be an aluminum flanged coupling welded or bolted to the basin, should be given special design consideration. In some installations, it will be desirable to attach aluminum or zinc anodes at the outlet to cathodically protect the adjacent basin interior surface because of the steel water-outlet pipe.

Copper piping should not be connected directly to the tower. Instead, a protector section of alclad aluminum or galvanized steel pipe at least six diameters in length or a minimum of one foot long should be inserted between the copper pipe and the tower. For the make-up water control, an aluminum or stainless steel float ball and rod should be used. Float valves of aluminum, trimmed in Type 18-8 stainless steel, with renewable seat of stainless steel are recommended. Heavily galvanized iron valves with stainless steel trim also are acceptable. Aluminum or stainless steel spray nozzles can be used.

Assembly

The aluminum alloys recommended above are well suited to standard shop practices for forming, joining and finishing. Where welding is required, the inert-gas-shielded arc methods are preferred. Aluminum sheet metal screws may be used in joining sheet members, but stainless steel screws are recommended for joining aluminum sheet to structurals of aluminum or to any steel member.

Although aluminum towers need not be painted, all joints should be sealed between faying surfaces during erection. For sealing aluminum to aluminum joints where gasketing is not required, the faying surfaces of both field and shop joints should be cleaned with a suitable solvent cleaner. A joint sealing compound is applied to one surface, and the assembly is made immediately. Any of the companies supplying sealing materials can recommend a suitable product for aluminum. Gasket materials for aluminum should be of the inert, non-absorbent type. Recommendations of gasket manufacturers should be helpful in making final selection.

In joints between aluminum and steel on the outside of the tower, such as where the tower rests on steel dunnage beams, the following procedure is recommended: the aluminum should be given one coat of a zinc-chromate primer complying with Army-Navy Specification JAN-P-735. The steel should be painted in the shop with a rust-inhibitive priming coat followed by field touch-up over which one coat of aluminum metal and masonry paint is applied.

If aluminum or steel motor housings or fan drives contact aluminum surfaces of the tower, the faying surfaces should be treated as the all-aluminum surface assemblies mentioned above.

For joints between aluminum and wood, the aluminum surfaces and through-bolts which will be contacted by the wood decking or fill should be protected. The metal surfaces should be cleaned with a solvent and coated with a heavy bodied bituminous paint. This procedure is not necessary for aluminum nails driven into redwood.

Any screwed pipe connections and bolts of inspection doors which may be removed periodically should be treated with a thread anti-seize compound meeting Specification JAN-A-669.

Painting

The unpainted exterior of the tower and the underside of the roof deck can be expected to have the same weather resistance as aluminum used architecturally. Laboratory data and field observations indicated that the interior of tower sidewalls constructed as recommended above are satisfactory without painting.

Field experience has indicated that painting the interior of the basin should be considered where there is no chemical water treatment or control of dissolved solids. Where alclad alloys are used, the coating of paint renewed at intervals will conserve the cladding as a safety factor. Also, painting permits the use of certain
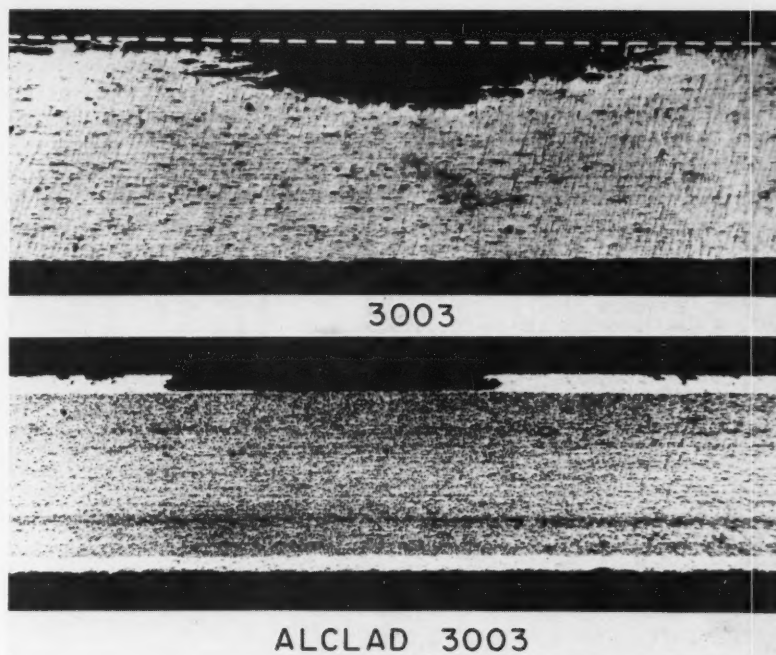
Figure 1—Photomicrograph showing the nature of corrosive attack on bare and Alclad 3003 sheet exposed to sea water for 22 months. Note the protection afforded the core metal by the cladding, limiting the depth of attack to the cladding thickness.

water treatments which otherwise might not be recommended. Some inhibitors, such as the chromates, are capable of limiting the protective action of alclad coatings.

Two painting procedures are recommended for aluminum cooling towers.

The first procedure is to (1) remove all grease and oil with a suitable solvent such as mineral spirits, (2) prepare the surface with a proprietary solution meeting the requirements of Military Specification MIL-QPL-5541-6 or with a washcoat primer meeting Military Specification MIL-P-15328 and (3) apply two coats of an aluminum paint made with a phenolic resin vehicle meeting the requirements of Military Specification MIL-V-1174.

A second procedure is to (1) remove all grease and oil with a suitable solvent and (2) apply three coats of a black bituminous material meeting Specification MIL-P-6883, following the directions of the paint supplier.

Field observations of aluminum fan blades show that baked-on, synthetic-resin enamels will maintain their initial smoothness for an extended period. For fan blades, a typical painting procedure is to (1) clean the parts with a solvent, (2) prepare the surface with a proprietary solution meeting the requirements of Military Specification MIL-QPL-5541-6 or apply a wash coat primer meeting Military Specification MIL-P-15328 and (3) apply two or three coats of a vinyl-resin base enamel in accordance with the recommendation of the manufacturer.

Water Treatment

Available data show that aluminum cooling towers in an all-aluminum system can be operated without water treatment in many localities. Since other materials of construction are usually present, the scope of the problem is enlarged to include the corrosion potential of all the individual materials of construction as well as their interaction. Another factor which must be considered is the concentration of dissolved solid impurities in an open recirculating system. Generally, concentration will increase the corrosion and scaling hazard for all metals.

Methods Employed To Study Water Treatments

A series of screening tests are used to evaluate treatments for specific water problems. Metallic specimens are immersed in jars containing the actual water to be employed or a synthetic water compounded to simulate the actual water. Where the possibility of galvanic corrosion exists, the metals are coupled and uncoupled in the container. After an arbitrary period of time (usually one week), weight-loss measurements, visual examinations and, in many instances, metallographic examinations are made on the specimens. The main advantage of this type of test is the simplicity of evaluating large numbers of waters under a variety of conditions with uniform testing procedure. With the results from such tests serving as a basis for comparison, various inhibitor combinations are added and the effectiveness of a projected treatment can be evaluated.

The second step is pilot testing. The type of experimental cooling tower used is illustrated in Figure 2. Specific details of their construction are given in Table 1. In operation the water passes downward through a 40-inch depth of untreated redwood lattice work consisting of ½ inch
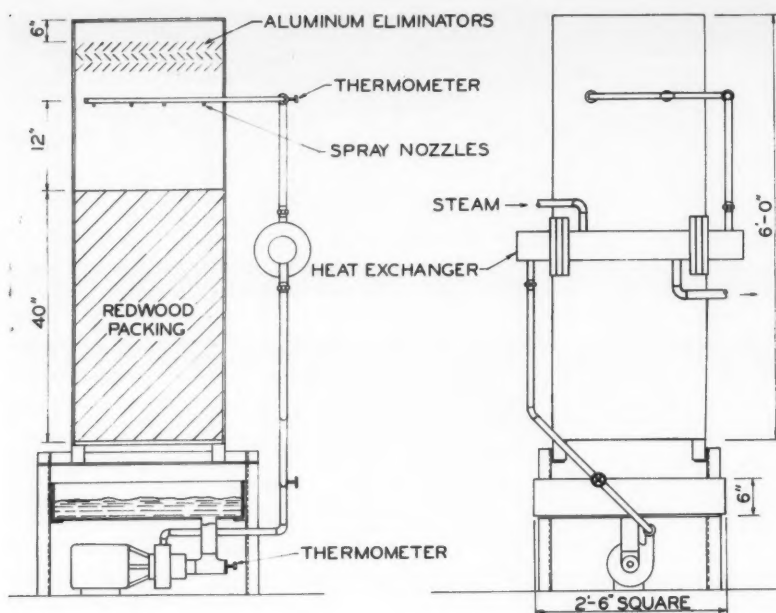
Figure 2—Laboratory cooling tower.

TABLE 1—Materials of Construction for Experimental Cooling Towers

Item	Description
Basin	Alclad 3003-H14
Eliminator Slats	Alclad 3003-H14
Framework	6061-T6 angle
Heat Exchanger	Steel shell, stainless tube sheets, Alclad 3003-H14 tubes and steel headers
Insulation	Rubber insulator between pipe from pump and basin
Pump	1½ in. Bell and Gosset
Pump Connections	2-in. iron pipe inlet, 1-in. iron pipe outlet
Spray Heads	Spraying Systems, Inc., Whirljet type B male connection ⅛ B10, ⅛-in. pipe size, ³⁄₁₆-in. orifice diameter, stainless steel construction.
Tower Fill	Redwood slats ½ in. by 1 in. by 24 in. spaced on 3-in. centers

TABLE 2—Average Composition of New Kensington Tap Water Over 12-Month Period

Total Solids	155-293 ppm
Chloride	5- 25 ppm
Sulfate	60-136 ppm
Calcium	16- 55 ppm
pH	7.0-8.0

TABLE 3—Range of Compositions for Pittsburgh Tap Water

Total Solids	103-179 ppm
Chloride	12- 33 ppm
Sulfates	55-195 ppm
Calcium	12- 45 ppm
pH	5.0-6.5

by 1 inch by 24 inch slats spaced on 3-inch centers. The air is drawn upward through the tower by means of a motor-driven blower mounted on top of the tower. Control of the air rate through the tower is achieved through a damper installed in the blower exhaust. Eliminator slats mounted just above the sprayheads reduce windage loss. Make-up water is metered into the basin through a ½-inch solenoid valve actuated by a float operated microswitch which controls the total volume of water in the system to within ± 0.3 gallon. Continuous purging is employed to maintain desired water concentration level. Electrodes installed in the blowdown line measure the pH of the

tower water and actuate a Beckman automatic titrator. Control of the chemical treatment is based on blowdown and is checked by periodic chemical analysis of the tower water. Continuous (gravity feed) and batch (manual) methods of adding chemical treatment have been used with success.

Resistance of Aluminum to Natural Waters

Corrosiveness of a given tap water on any of the common materials of construction is difficult to predict since no exact correlations are known between such items as chloride content, sulfate content,

total solids, total hardness, total alkalinity, etc.

For practical purposes, natural waters may be divided into four main classifications:

1. Waters containing heavy metals such as copper, nickel and lead.
2. Neutral or nearly neutral waters.
3. Acid waters.
4. Alkaline waters.

Waters Containing Heavy Metals

Aluminum alloys may be susceptible to some pitting when certain heavy metals such as copper are present, particularly in acid waters. Alkaline waters containing copper are less corrosive. This decrease in corrosion correlates with the decrease in soluble copper ion as shown in Figure 3 when a total of 5 ppm of copper was added to the solution. Increased concentration of anions and cations in open, recirculated cooling water can affect this copper ion-pH relationship in the pH range 5.0 to 8.0. Alclad products resist perforation in waters containing heavy metals and generally are recommended for recirculated water applications.

Neutral or Nearly Neutral Waters

Service and laboratory experience have indicated that neutral waters (pH 6.0 to 8) have little or no action upon aluminum.[1] Factors that can alter this situation without changing the pH significantly are the presence of heavy metals or excessive concentration of particular water components. The corrosion resistance of aluminum to once-through natural waters has been shown effectively in an experimental all-aluminum hot and cold water distribution system. In this instance New Kensington, Pa., tap water flows through the pipes with a pH of 7.0 to 8.0 and has the composition given in Table 2. Up to the present time, the Alclad 3003 pipe employed in this system (23 years service) has given trouble-free performance.

In an open recirculating system, however, the problem of predicting the degree of corrosion is difficult because of the effects of concentration of certain anions and cations.[2] In this connection the corrosion of the aluminum may be a function of the degree to which the water scales or builds up deposit since an oxygen concentration cell may be formed under the deposit resulting in a pit. One of the common methods of minimizing scale is to retain the pH acid plus some organic dispersive agent or chelating agent or both. If heavy metal contamination (such as soluble copper) is also present, some compromise (slightly alkaline) pH may be employed where the soluble copper will be precipitated. Another alternative with copper present is to add an inhibitor which can prevent corrosion of copper or complex the soluble copper or both. For this purpose sodium mercaptobenzothiazole has been used advantageously.

The solution potential relationships among the metals present in a system may be altered by a change in the water composition. In certain cases, it may be desirable to electrically isolate dissimilar
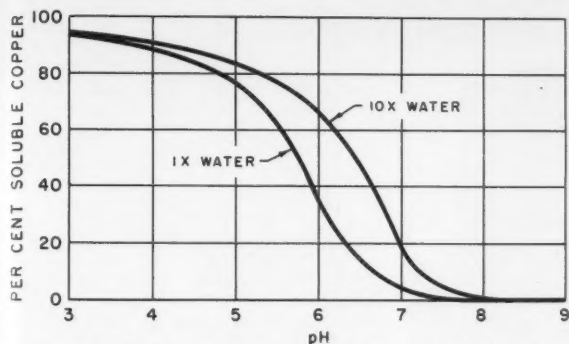
Figure 3—Solubility of copper in water at various pH's based on the total addition of 5 ppm of copper.

Figure 4—Variation in corrosion with variation in polyphosphate-calcium ratio.

metals, to install galvanic anodes of aluminum or zinc or to employ replaceable sacrificial aluminum sections between the aluminum and the more cathodic metals.

Acid Waters (pH 4.5 to 6.0)

Aluminum alloys are resistant to waters down to a pH of 4.5 even in the presence of large amounts of chloride. Since waters of such low pH would seldom, if ever, be used in a cooling tower, the problems presented by such waters are academic. Raising the pH to the near-neutral range would be mandatory for steel and copper and beneficial for aluminum because the corrosion of more cathodic metals such as steel and copper would be reduced. Where the pH is still low enough to give some copper corrosion, the use of an inhibitor to minimize copper corrosion or to complex the copper in solution should be employed for the benefit of both steel and aluminum parts in the system.

Alkaline Waters (pH 8.0 to 9.0)

Aluminum alloys are generally serviceable for use with waters containing metals of the alkali or alkaline earth series having a pH range of 8.0 to 9.0. Alkaline waters in this range may darken the surface of aluminum alloys, but the amount of attack is usually insignificant in terms of metal weight loss.

One of the most troublesome consequences of alkaline cooling waters, especially in open recirculated systems, is the problem of scaling. The increased concentration of hardness components can result in precipitation of calcium or magnesium carbonate or both on the metal surfaces in the system, regardless of the material of construction. Similarly, phosphate treatment can result in precipitation of the phosphates of calcium and magnesium. Two steps are usually taken to minimize this latter type of scale. The first is to lower the pH of the water to the range of 6.0 to 6.5. The other step is to add the phosphate as polyphosphate which forms a relatively soluble product with alkaline earth cations even at slightly alkaline pH values. Addition of polyphosphate to prevent scaling, however, is only partially effective since the rate of reversion of polyphosphate to orthophosphate is rapid. It has been found by analyses that a recirculated cooling tower water with polyphosphate treatment will contain from 50 to 75 percent orthophosphate at

any particular time. If the water treatment is inadequately protecting the metals in the cooling system, deposition of the phosphate salts of these metals will aggravate the scaling problem.

Types of Water Treatment

The problems of corrosion in open recirculating cooling water systems is one to which considerable research has been devoted in recent years. High concentrations of corrosion inhibitors with resulting high treatment costs are no longer necessary. Because the majority of cooling towers and heat exchangers in the past have been fabricated from materials of construction other than aluminum, the majority of the water treating companies have had little experience with aluminum for this application. The use of aluminum does not introduce any new or unique water treatment problems. In fact, the major concern is that other metals in the system be adequately protected so that they do not cause corrosion of the aluminum by contaminating the aluminum surface.

The presence of oxygen is beneficial to aluminum because it can repair weak points in the oxide film, but oxygen is corrosive to steel in the absence of an inhibitor. Similarly the presence of carbon dioxide has no effect on aluminum but is corrosive to unprotected steel and copper. Often cooling tower waters may be contaminated with hydrogen sulfide where that gas is present in the atmosphere. Once again aluminum is virtually unaffected in contrast to steel and copper. In a discussion of water treatment for contact with aluminum cooling towers and heat exchangers, few new concepts need to be introduced.[3]

The most frequently employed corrosion inhibitors for cooling water systems are the chromates and polyphosphates.[4, 5, 6] These may be used to treat water contacting aluminum. Service information available on treatment of aluminum systems deals mainly with orthophosphate and polyphosphate type treatments since the use of chromate is often restricted. This does not mean that chro-

mates do not inhibit corrosion of aluminum. On the contrary, chromates have been employed for many years in closed recirculating systems built of aluminum. Similarly, chromate-phosphate mixtures have been employed successfully in closed recirculating systems. Chromate is such an effective filming agent on aluminum that it can completely inhibit the action of phosphoric acid on aluminum. Such a solution is used as a standard treatment for removing films or products of corrosion from aluminum with negligible attack of aluminum.[7]
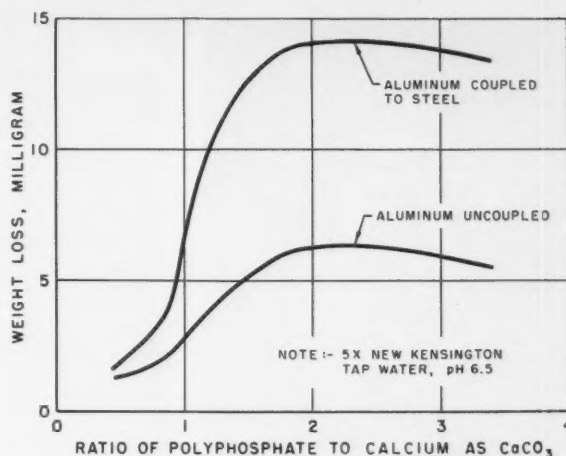
The two water treatments which have been studied most closely utilize polyphosphate and orthophosphate. Both of these treatments have been used in pilot laboratory cooling towers of all-aluminum construction with redwood fill. Subsequently, the treatments have been field tested in air-conditioning systems with aluminum cooling towers in an office building in Pittsburgh, Pennsylvania, and with heat exchanger tubes in a laboratory building.

The first treatment is a polyphosphate-type proprietary water treatment which has given satisfactory service at the office building. The level of effective concentration has been about 35 ppm of PO_4 with a pH of 6.0 to 6.5. The cooling waters are concentrated about 5 times. The composition of Pittsburgh tap water is given in Table 3. More concentrated cooling water (up to ten times) may be employed if economic considerations dictate. One important condition for the use of polyphosphates should be stressed. The ratio of polyphosphate to calcium hardness expressed as $CaCO_3$ must be less than two for satisfactory inhibition. Although first considered necessary for the protection of steel,[8] this condition appears to be equally valid for aluminum as shown in Figure 4.

The second treatment has been developed for multi-metallic systems of aluminum, steel and copper. This treatment is also a phosphate-type treatment containing additional chemical agents. The additives have a synergistic effect on the phosphate which generally prevents corrosion of metals by water and can minimize corrosion of copper or complex
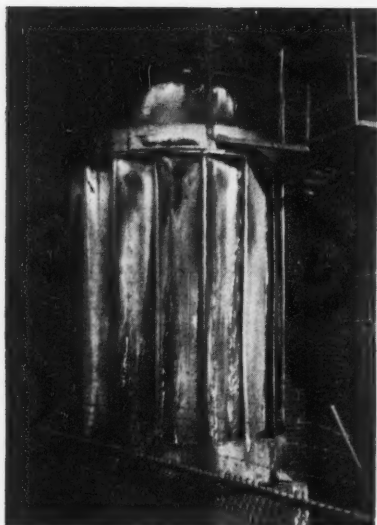
Figure 5—Aluminum cooling water tower that has operated 26 years on treated water.
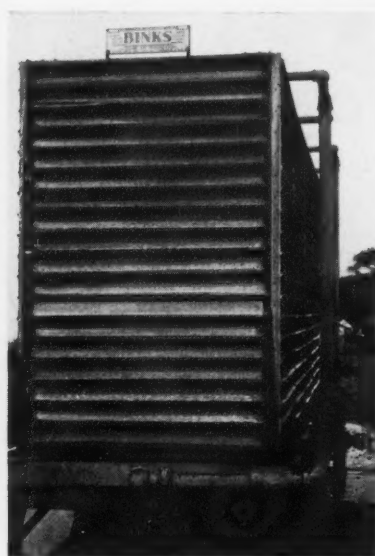
Figure 6—Aluminum cooling tower operating since 1937 on non-treated water with no protective paint.
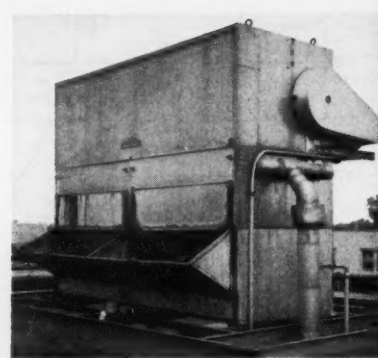
Figure 7—All-aluminum 55-ton cooling tower with aluminum fill. This tower operates in conjunction with an air-conditioning system designed to contain aluminum, steel and copper parts. An orthophosphate plus additives water treatment, designed for such multimetallic systems, has given satisfactory results.

copper ion already present in solution. This treatment has given gratifying results in the laboratory building's air-conditioning system and attendant all-aluminum cooling tower. The operating level of this inhibitor is about 10 ppm of PO_4 and 3 to 5 ppm of additives. The water used in this system is about five to ten times as concentrated as New Kensington tap water (see Table 2) and the pH has been 7.0 to 7.5.

In conjunction with the search for new inhibitor combinations, a research program has been instituted to study the characteristics and performance of aluminum fill for cooling towers. The fire hazard of redwood fill and consequent high insurance rates have induced manufacturers to consider the use of metal fill. In studies to date, the performance of aluminum fill has been satisfactory.

Bactericides

The use of compounds containing heavy metals such as copper or mercury should be avoided because they will accelerate the corrosion of many commercial metals and alloys. Aluminum can be used with most bactericides as far as compatibility with aluminum is concerned. Chlorine is commonly employed and would be preferred with aluminum. Chlorination to a residual of 0.5 ppm with chlorine gas or calcium hypochlorite has been used successfully. An alternative treatment is periodic addition of pentachlorophenate or a mixture of trichlorophenate and pentachlorophenate. The high alkalinity of these chlorophenate salts can be lead to some precipitation from a phosphate solution. This occurs regardless of whether the phosphate is present as orthophosphate or phosphate. The addition of pentachlorophenate several times a week rather than a single large addition is recommended to minimize precipitation and consequent deposition on heat-transfer surfaces. Chlorinated amines also tend to

precipitate phosphate because of the high pH of their solution.

Field Experience

Many aluminum cooling towers are in service today. Some of the aluminum towers to be mentioned here were designed according to the recommendations made in this paper.

A 26-year-old cooling tower operating at a transformer substation in Pittsburgh, Pa., is shown in Figure 5. Alloy 3003 was used without paint. This tower operated for five years on untreated water. Corrosion occurred, and a schedule of water analyses and inhibitor additions were instituted. No shutdown time for maintenance was required at that time or since because treatment was effective in alleviating the corrosion.

A tower that has operated in Cleveland, Ohio, since 1937 is shown in Figure 6. It, also, was not painted, but no water treatment has been required since periodic inspections have not shown any corrosion.

Four towers designed to the recommendations given in this paper are of specific interest. The 1250-ton redwood-filled aluminum tower used in the air-conditioning system of an office building in Pittsburgh, Pennsylvania, was one of the first towers to use Alclad 3004 sheet. It has operated since 1954 with the proprietary polyphosphate-type water treatment referred to previously.

Another aluminum cooling water tower operating with redwood fill is also in Pittsburgh. The tower was constructed with alclad aluminum alloys, left unpainted and operated with untreated water. A copper tubed air-conditioning condenser was used in conjunction with this tower. After one year's operation the aluminum tower was in good condition, showing little corrosion.

An all-aluminum tower with aluminum fill, located at a research laboratory in New Kensington, Pennsylvania, is shown in Figure 7. A study of water treatment in a multi-metallic system was conducted on this tower by connecting a copper tubed condenser. Alclad 3003 sheet and 6061-T6 structurals were used for the construction. The phosphate-type treatment developed specifically for this tower has been employed for two years with satisfactory results. Another 55-ton tower, in Atlanta, Georgia, also has a copper tubed condenser. The effect of a chromate-polyphosphate treatment on this tower is currently being studied.

In a survey of manufacturers who have used aluminum in cooling tower construction, it was found that aluminum offered several advantages. Those advantages mentioned most often were resistance to corrosion in a wide variety of waters; light weight, which reduces the cost of fabrication, shipping and erection; and maintenance of good appearance in both industrial and seacoast environments.

Research and development in problems related to handling various waters in aluminum will continue. However, the performance record of properly designed aluminum towers, the economic advantages, and the present knowledge of water treatment indicate that aluminum cooling towers are now ready for full consideration by the industry.

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A Critical Analysis of Pitting Corrosion*

By N. D. GREENE and M. G. FONTANA

Introduction

PITTING CORROSION probably ranks second only to stress corrosion cracking in its destructive and insidious nature. It is unusually destructive because perforation by a single pit can cause complete equipment failure. The practical necessity of preventing pitting attack, coupled with the inherent difficulties in studying this form of corrosion, has led to numerous misconceptions concerning its mechanism and behavior.

This paper attempts to analyze critically the results, conclusions and experimental techniques of various investigators on the basis of modern electrochemical and corrosion theories. Although the emphasis is primarily on the pitting of stainless steel alloys, most of the conclusions can be applied to the pitting corrosion of other metals and alloys.

This fundamental study of pitting was instigated by the Alloy Casting Institute.

General Aspects

Definition of Pitting

Pitting is an example of highly localized corrosion. The attack is limited to extremely small areas of the metal surface while the remaining surface is relatively unaffected. Pits start at small points on the surface and enlarge with time. However, the enlargement of the surface area of a pit is small in comparison with its increase in depth and volume.

Champion[1] has divided corrosion into two main classes, general and localized, and has further subdivided these classes according to the general scheme shown in Figure 1. Champion further defines pitting as follows:

"The term pitting is used when the area of attack is so localized that the width is of the same order as or less than the depth of attack (the dividing line between pitting and uneven local corrosion may be taken at a width/depth ratio of about 6)."

Hence, there is a continuous gradation between general corrosion and localized corrosion, and there is no distinct surface structure that can be designated as pitting attack. Any definition of pitting based on surface appearance must be purely arbitrary; the limiting width/depth ratio quoted above could be chosen as two or ten instead of six.

Another problem in the characterization of pitting is the lack of distinction between it and crevice corrosion. Crevice corrosion or concentration cell corrosion
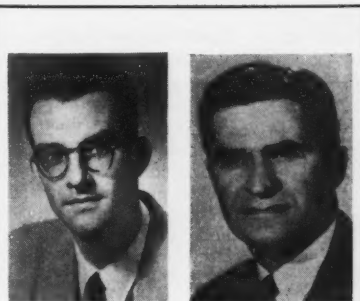
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is attack that is restricted to shielded areas or crevices on the exposed metal surface. Crevice corrosion, because of its localized nature, usually appears as pits or perforations. Almost any electrolyte is capable of supporting crevice corrosion, whereas only specific environments can cause localized attack on freely exposed surfaces. To differentiate between pitting corrosion and crevice corrosion, the following criterion is suggested: Crevice corrosion is attack that is limited to surface areas shielded from direct exposure to the electrolyte, regardless of the surface structure produced by the attack.

Since there is no generally accepted definition of pitting corrosion, this term obviously includes a wide variety of corrosion phenomena.

Factors Influencing Pitting

Metallurgical Factors

As a class, the stainless steel alloys are more susceptible to damage by pitting corrosion than any other group of metals or alloys. As a result, numerous alloy studies have been devoted to im-

Abstract

A critical analysis of the literature on pitting corrosion published during the past 35 years is presented. The definition of pitting and the factors influencing this type of attack are considered. An examination of the theories of pitting corrosion and the methods used to study this form of corrosion are also included.   3.2.2

proving the pitting resistance of stainless steels[2-10] and are summarized in Table 1.

Holding Types 304 and 316 stainless steel in the sensitizing temperature range (900-1600 F) decreases their pitting resistance.[2, 9] Austenitic stainless steels exhibit the greatest pitting resistance when solution-quenched above 1800 F.

Severe cold-work increases the pitting attack of 18 percent chromium-8 percent nickel stainless steels in ferric chloride.[9] Preferential edge pitting is usually observed on most wrought stainless products.

Surface finish often has a marked effect on pitting resistance. Pitting and localized corrosion are less likely to occur on a polished than on etched or ground surfaces.[4, 9, 11] Generally, the pits that form on a polished surface are larger and penetrate more rapidly than those on rough surfaces.

Solution Composition

The halides and halogen-containing anions are almost always associated with the pitting of metals and alloys. Chlorides, bromides and hypochlorites are the most aggressive of the halogen-containing anions. Fluorides, iodides, and iodine-containing anions are practically without pitting tendencies. Because of the present ambiguous definition of pitting, it is difficult to determine which of the anionic species, other than halides, can cause pitting corrosion.

Of the cations, the oxidizing metal ions produce the worst pitting attack. Ferric, cupric and mercuric halides are the most aggressive of all pitting reagents. The non-oxidizing metal halides such as aluminum, calcium and sodium also cause pitting although to a lesser degree than oxidizing metal halides.

Pitting attack can be prevented or inhibited in many instances by the presence of hydroxide,[12] chromate[13] and silicate[14] salts. Perhaps the most striking example of pitting corrosion inhibition is the action of nitrate additions to ferric chloride solutions. Uhlig[9] observed 18 percent chromium-8 percent nickel stainless steel immersed in 10 percent ferric chloride containing 3 percent sodium nitrate did not pit but corroded uniformly at a rate of 2 mpy. Without nitrate the corrosion rate with pitting was a million times greater.
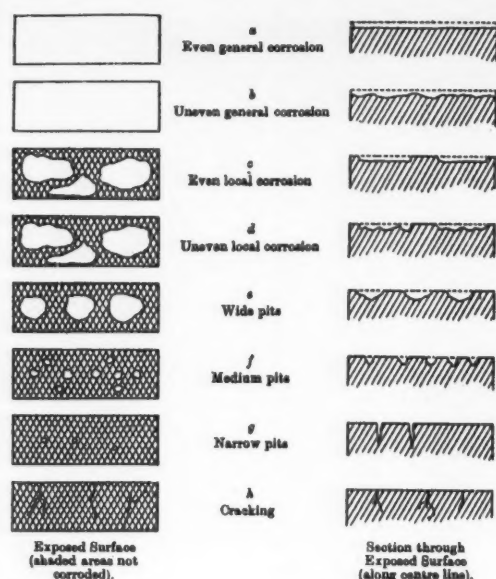
Figure 1—Types of corrosion.

Loci and Distribution of Pitting

There is considerable controversy about pits' origin on a metal surface. For stainless steels, the fact that increasing carbon content and holding in the sensitizing temperature range causes decreased pitting resistance leads to the assumption that carbide particles might act as pit nuclei. However, Uhlig[9] found that pits readily formed on an 18 percent chromium-8 percent nickel stainless steel containing only 0.001 percent carbon. A sensitizing heat-treatment markedly reduced the resistance of this alloy. Apparently, carbides do not act as pit nuclei. Also there is no preferential pitting at the normal oxide and silicate inclusions in stainless steels.[4, 6, 9] Electron microscope studies of pitted aluminum surfaces likewise indicated no preferential pit sites.[15]

During electrolytically accelerated pitting tests in various chloride solutions, Streicher[4] observed that pitting occurred preferentially at grain boundaries, and especially at boundary intersections. Standifer,[16] using ferroxyl indicator, observed that pit sites occurred randomly on stainless steel alloys. Upon the application of small anodic currents, the number and size of these pit sites increased. At higher current densities, pit sites appeared preferentially along grain and twin boundaries. Thus, Streicher's observations appear to be due to the specific action of externally applied currents. However, the validity of the ferroxyl test is open to question (See section on study methods) and cannot be taken as positive proof. Pits occur almost randomly with respect to surface structure with a preference for grain and twin boundaries.

This distribution of pitting has been studied by numerous investigators using statistical analysis.[17-23] The experiments of Mears and Brown[18] and Aziz and Godard[21] demonstrated that corrosion pits are not mutually independent events, and that pits interact with one another. This interaction is believed to be caused by the cathodic protection of the metal surface immediately adjacent to a pit site.[18, 21, 24]

In summary, pits are nearly random with respect to surface structure, whereas they are not random with respect to each other.

Electrochemical Aspects

Cathodic Reactions

Oxygen reduction, hydrogen evolution, and metal ion reduction are the three most important cathodic reactions in corrosion processes. Of these, oxygen reduction and metal ion reduction are the cathodic reactions usually associated with pitting corrosion; hydrogen evolution is rarely observed.

Oxygen reduction can proceed along two possible paths:[25]

acid solution:
$$O_2 + 4H^+ + 4e = 2H_2O \qquad (1)$$

alkaline solution:
$$O_2 + 2H_2O + 4e = 4OH^- \qquad (2)$$
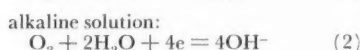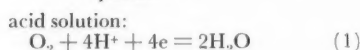
The solubility of oxygen in water is very low; in electrolyte solution it is even less. Hence, the velocity of corrosion involving oxygen reduction is highly dependent on the diffusion rate of oxygen to cathodic sites. Any factors which influence oxygen diffusion rate will influence the velocity of corrosive attack.

Metal ion reduction is unique in its effect on pitting. Corrosives containing reducible metal ions often show extremely aggressive pitting tendencies. For solutions containing cupric or ferric ions, the cathodic reactions are

$$Cu^{+2} + e = Cu^+ \qquad (3)$$

$$Fe^{+3} + e = Fe^{+2} \qquad (4)$$
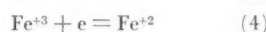
Uhlig[6] determined the pitting tendencies of various metal halides toward 18 percent chromium-8 percent nickel stainless steel and found pitting intensity was related to the standard oxidation-reduction potential of the metallic ions. His results are presented in Table 2. All these solutions are capable of pitting stainless steels in the presence of dissolved oxygen. However, metal halides with sufficiently high oxidation-reduction potentials can pit stainless alloys in the absence of dissolved oxygen and are practically unaffected by changes in oxygen supply.

There is considerable confusion in the literature as to the effects of environmental changes on pitting velocity. The effects of temperature, electrolyte concentration and dissolved oxygen are not defined clearly. This confusion may be resolved by relating pitting behavior to the particular cathodic reaction which occurs. Table 3 summarizes the predicted and observed behaviors of pitting attack in oxygen and metal ion reduction systems. The maximum point phenomenon in oxygen reduction systems was first predicted by Asselin and Rohrman[26] who recognized that solution conductivity increases with increasing temperature and concentration; oxygen solubility decreases under these conditions. Uhlig and Morrill[27] found such maxima during studies of the pitting of 18 percent chromium-8 percent nickel stainless steel by sodium chloride. Pitting involving metal ion reduction is independent of oxygen supply and, therefore, shows no maximum point phenomenon.

Anodic Reactions

The anodic reaction during pitting is the solution of the metal as ions:

$$M = M^{+n} + ne \qquad (5)$$
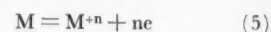
where n represents the charge of the metallic ion.

During pitting attack, there is a tremendous increase in chloride ion concentration within pit cavities due to ionic migration. Also the pH of pit interiors is much lower than the surrounding solution due to the hydrolysis of the chloride salts contained within them. These changes have been observed during the pitting of iron,[28, 29, 30, 31] aluminum[19] and 18 percent chromium-8 percent nickel stainless steel.[6]

The corrosion pit is a unique type of anode. The first indication of its unusual nature was discovered by Evans[32] who observed that on vertically immersed specimens, pits tended to form in vertical rows, indicating that the corrosion products flowing from a pit stimulated corrosion at other points. Uhlig[6] has also demonstrated the activating action of pit corrosion products.

The term autocatalytic was introduced by Edeleanu and Evans[33] and Evans.[34] Autocatalytic refers to the fact that the corrosion processes within a pit produce

TABLE 1—Effects of Alloying on Pitting Resistance of Stainless Steel Alloys[2-10]

Element	Effect on Pitting Resistance
Chromium	Increases
Nickel	Increases
Molybdenum	Increases
Silicon	Decreases; increases when present with molybdenum
Titanium and Columbium	Decreases resistance in FeCl₃; other media no effect
Sulfur and Selenium	Decreases
Carbon	Decreases, especially in sensitized condition
Nitrogen	Increases

TABLE 2—Pitting Tendencies of Metal Halides[10]

Solution (0.5M)	E_o (Standard)	Presence of Pits
FeCl₃	+0.77	yes
CuCl₂ (Cu⁺² + Cl⁻ = CuCl)	+0.57	yes
SnCl₄	+0.15	no
NiCl₂ (no lower valence salt)	0.00	no
TiCl₄ in 0.5M HCL	−0.04	no
CrCl₃	−0.4	no

conditions which are themselves both stimulating and necessary for the continuing activity of the pit. These conditions obviously are those that exist within a growing pit, namely, high chloride ion concentration and low pH.

As a result of the autocatalytic nature of pitting, newly formed pits are very unstable and often become inactive because the inward migration of chloride ions is insufficient to offset the loss of pit corrosion products by diffusion and convection. Aziz[22] found that one half the pits initially formed on an aluminum surface exposed to tap water became inactive in two weeks. Many of the artificial pits of copper used by May[35] were erratic and often became inactive during the early stages of their growth. The erratic initial corrosion rates of Type 304 stainless steel in ferric chloride, observed by Liebhafsky and Newkirk,[36] may also be an example of this phenomenon although this was attributed to possible experimental errors.

Electrochemical Control

Considerable effort has been devoted to the determination of the type of electrochemical control operating during the pitting corrosion of stainless steels. The conclusions of the various investigators are contradictory. The type of electrochemical control is dependent on the electrode reactions and, therefore, on the type of corrosive to which the alloy is exposed. In the case of non-oxidizing metal halides, Ellis and LaQue[37] and Brown and Mears[38] have concluded that the localized attack of 18 percent chromium-8 percent nickel stainless steels exposed to sodium chloride is cathodically controlled. For the same system, Standifer[16] has proposed the unique hypothesis that the pitting attack is initially under anodic control but shifts to cathodic control as the attack progresses. This shift in control was attributed to the decrease in total cathodic area as the anode or pit area increased and consumed it. For ferric chloride, an oxidizing metal halide, Brown and Mears[38] indicated that the pitting attack of 18 percent chromium-8 percent nickel stainless steel in this medium is anodically controlled; Liebhafsky and Newkirk[36] argue that it is cathodically controlled.

There is an inherent, unrecognized anomaly in the electrochemistry of pitting corrosion caused by the autocatalytic nature of the pitting process. Under steady-state, open-circuit conditions, there will be no potential difference between a pit and the remaining metal surface. This can be readily seen by noting that under conditions of zero current flow there will be no migration of chloride ions to the pit site. If steady-state conditions are achieved, the composition of the solution in contact with the pit interior will be identical to that in contact with the remaining metal surface.[1] Thus, since the metal and solution at

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[1] Actually, this only applies to the ideal case in which the diffusion rates of ionic species at both areas are equal. Shallow corrosion pits containing no re-entrant surfaces will closely approach this ideal case.

both areas have identical compositions, there can be no potential difference between these areas.[2] As a result of this anomalous behavior, pitting corrosion cannot be completely described by the usual steady-state polarization curves employed in corrosion studies. The concept of electrochemical control must be modified when applied to pitting attack. Thus, the electrochemistry of pitting appears more complex than is commonly believed. These problems are considered elsewhere.[39, 40]

Theories of Pitting Corrosion

The following is a discussion, in chronological order, of the various theories and concepts used to explain the phenomenon of pitting attack. Several of the subsections are not actual theories but merely collections of similar ideas grouped together for purposes of organization.

Imperfection Theory

In 1920, Seligman and Williams[41] advanced what may be termed the imperfection theory to explain the pitting corrosion of aluminum. The authors stated that pitting would occur only if crevices or subsurface cavities were originally present in the metal. They also postulated that an autocatalytic reaction involving hydrogen peroxide occurred within corrosion pits.

The autocatalytic mechanism proposed by the authors is not possible. The importance of microscopic surface fissures as pit sites has been indicated by Wulff, as reported by Uhlig.[6] Although surface cracks and imperfections can undoubtedly act as starting points for pitting attack, recent experiments such as electron microscope studies[15] indicate that pits probably can form independently of surface irregularities.

Peptization Theory

The peptization theory of pitting attack was proposed by Evans[42] in 1922 to explain the pitting tendencies of halide salts. Peptization refers to the transformation of a bulk precipitate to a colloid suspension. Halide ions are capable of peptizing many substances, including ferric oxide. Assuming the passivity of iron was due to a surface oxide layer, Evans proposed that chloride ions

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[2] This is based on the assumption that the metal has a homogeneous composition.

could destroy this layer at isolated points and allow attack to occur. A serious objection to this theory is that it is based on a concept of passivity which has yet to be proven conclusively.

Penetration Theory

In 1927, Evans[43] suggested that the specific pitting tendency of chloride ion was due to its small diameter which permitted it to penetrate the protective oxide layer of iron. This theory was brought into prominence in 1930 by the experiments of Britton and Evans.[44, 45] The authors applied a potential of two volts between two aluminum plates immersed in potassium dichromate solution containing additions of various salts and measured the resulting current flow. The magnitude of the current flow for the various salt additions decreased in the order

$$KCl > KBr > KI >$$
$$KF > K_2SO_4 > KNO_3 > Na_3PO_4$$
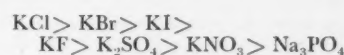
The authors noted that this series closely paralleled the corrosivities of the salts and concluded that the observed current flows were a direct measure of the abilities of the various anions to penetrate the protective oxide layer on aluminum surfaces.

Close scrutiny of the experimental technique of Britton and Evans shows that it is not a critical experiment, neither proving or disproving the concept of ion penetration. The observed current flows represent the metal dissolution rate and not the leakage or penetration of ions through an oxide layer.

The penetration theory was effectively refuted by the work of Burwell and May[46, 47] in 1948. These investigators measured the permeability characteristics of oxide films isolated from aluminum surfaces. Diffusion, osmosis and electrical resistance measurements demonstrated that potassium chloride and potassium nitrate solutions penetrated the oxide films at almost identical rates. Burwell and May concluded that the exceptional corrosive action of chloride ion could not be the result of any special penetrating ability.

Adsorption Theory

The adsorption theory of pitting be-

TABLE 3—Effect of Cathodic Reaction on Pitting Behavior of 18-8 Stainless Steel

	Oxygen Reduction	Metal Ion Reduction
Examples	NaCl, NaBr, CaCl₂, MgCl₂, AlCl₃	FeCl₃, FeBr₃, CuCl₂, HgCl₂
Relative Rate of Pitting Attack	Slow	Moderate to rapid
Increasing Temperature	Corrosion rate increases, then decreases. Maximum point.	Corrosion rate increases. No maximum point.
Increasing Chloride Concentration	Corrosion rate increases, then decreases. Maximum point.	Corrosion rate increases. No maximum point.
Increasing O₂ Content	Increases attack	Negligible effect
Effect of pH	Low pH—general attack; neutral pH—pitting; high pH—no attack	Solutions stable only at low pH. Neutral and high pH—no attack
Corrosion products	Usually insoluble	Usually soluble

came prominent during 1945-47, notably due to the work of Ershler,[48] Hickling[49] and Kabanov, Burstein and Frumkin.[50] In general, the adsorption theory postulates that pitting attack begins because chloride ions displace adsorbed oxygen or prevent it from adsorbing at isolated points on a metal surface. One of the theories of passivity postulates that adsorbed oxygen protects the metal surface from attack. According to the adsorption concept, the passive state is destroyed by the preferential adsorption of halide ions. Like the peptization theory, an objection to the adsorption concept is that it is based on a particular, unproven theory of passivity.

Acid Theory

All of the preceding theories are aimed primarily toward an explanation of the onset of pitting attack. With the exception of the imperfection theory, none of them detail the mechanism of pit growth. The acid theory of pitting was the first to describe a complete mechanism for pitting corrosion.

The acid concept was formalized in 1947 by Hoar,[51] who postulated that pitting corrosion is caused by pH changes that occur at anode areas. During corrosive attack in chloride solution, the chloride ions migrate to anode areas and increase the acidity at these regions. If the pH is low enough, the metal will dissolve as a soluble salt instead of precipitating as metal oxide or hydroxide. Apparently, this is an autocatalytic mechanism because increasing the acidity at anode regions increases the rate of anodic dissolution which, in turn, causes a further increase in acidity.

This theory can be extended to explain the onset of pitting attack as stated by Evans:[34]

"Imagine a piece of metal placed in a solution of pH value high enough to make the discharge of hydroxide ions the main reaction. If, for any reason, anodic current density is momentarily high at one particular point, it produces conditions increasingly favorable to the formation of soluble products. This attack at this point becomes permanently faster than at places where film conditions to thicken and protect the metal."

Hoar[51] attributed the extreme corrosivity of the halide ions to the high strengths of their free acids as compared to other anionic species. Thus, halide ions would be expected to produce greater acidity at anodic areas than other anions such as sulfate. On the basis of this theory, Hoar[52] predicted that perchlorate ions should be similar to chloride ions in their corrosion tendencies toward iron since perchloric acid is the strongest of all acids. Experimental results indicated that his prediction was correct; chloride and perchlorate ions showed identical pitting tendencies under certain conditions.

The acid theory provides a plausible mechanism for pitting corrosion. Today, it is the most generally accepted theory of pitting attack. It has been used to explain the pitting of aluminum,[19,33,34,55] iron[34] and stainless steel.[4] Although the

acid theory has been used usually in conjunction with the oxide film theory of passivity, this concept of passivity is not an essential assumption in the theory. Metallic passivity is destroyed in nonoxidizing, highly acidic environment containing halides.[6] Thus, the acid theory is valid, independent of passivity mechanism.

A major criticism of the acid theory is that the differences in the strengths of the various acids do not appear to be sufficient to account for the tremendous differences in the corrosion behaviors of the various anions. Also, predictions based on the theory are questionable since the relative strengths of free acids are in doubt.[54]

Ion Exchange Theory

Consideration of the pitting theories discussed thus far shows that all lack a truly fundamental explanation of the pitting tendencies of the halide ions. The halide ions show unique behaviors in many phenomena, such as ion exchange reactions, complexing tendencies, adsorption, electrodeposition and acid strength behavior. The pitting tendencies of the halides probably is not a separate and distinct property but is in some way related to the other unique properties of these ions. A fundamental explanation of the corrosion behavior of the halides should also explain these other properties.

Piontelli[55] advanced in 1950 what may be called the ion exchange theory in an attempt to fundamentally explain the corrosion behaviors of the various anionic species. This theory is not a theory of pitting attack but a general concept which can be applied to pitting. Piontelli postulated that the influence of anions on electrochemical processes is primarily a result of their catalytic effect on electrode ionic exchange reactions; they affect electrode reactions without being consumed by them. According to the theory, the catalytic influence of anions is essentially determined by their polarizabilities or deformabilities.[55,56] Highly polarizable anions, such as the halides, catalyze or accelerate electrochemical ion exchange processes; non-polarizable anions, such as perchlorate or sulfate, retard these processes.

The ion exchange theory proposes a direct relation between anionic polarizability and corrosive tendency. Highly polarizable anions show pronounced corrosivities toward most metals, whereas weakly polarizable anions tend to retard or inhibit corrosive action. Perchlorate, the least polarizable of all anions, would be expected to show the least catalytic influence on electrochemical processes and corrosion. This prediction is supported by the polarization studies of Piontelli and Poli.[57,58] However, the acid theory with corrosion studies by Hoar[52] indicates that the perchlorate ion is a very aggressive corrosive. Thus, the acid theory and the ion exchange theory are diametrically opposed as to the corrosion behavior of the perchlorate ion. The validity of these two theories depends on the correctness of their predictions regarding perchlorate ion.

An objection to the ion exchange theory, especially when applied to pitting corrosion, is its lack of sufficient experimental evidence. The importance and extent of anionic catalytic action on the various electrode processes are unknown. Also the theory, because of its generalized nature, does not detail the mechanisms that operate during pitting attack.

Other Theories and Concepts

Magnetic Theory

Studies of the pitting of iron and steel by water led Ackerman[59] to the conclusion that the localized attack was caused by magnetic poles on the metal surface. These magnetic poles were believed to be induced in ferrite patches by the earth's magnetic field. Although Ackerman's concept of pitting corrosion seems rather dubious, it does suggest an interesting idea in regard to the pitting of non-magnetic ferrous alloys such as the austenitic stainless steels. Ferrous and ferric salts are highly paramagnetic and are attracted strongly by magnetic fields. Hence, the ferrous salt corrosion products during exposure to a pitting corrosive would be expected to accumulate at any magnetically permeable areas on an austenitic stainless steel surface and thus promote pitting at these points. This may be a possible explanation of the lower pitting resistances of ferrite-containing stainless alloys.[4,6]

Screening Effects

All of the theories of pitting attack overlook an important aspect: the stability of a growing pit. Pits grow in the presence of dissolved oxygen, oxidizing metal cations such as ferric and cupric ions, and inhibiting anions such as chromate, nitrate and carbonate. New pits often become inactive probably because passivating or inhibiting species in the corrosive enter the pit interiors. However, the fact that many pits remain active in the presence of these reagents suggests that some sort of screening mechanism must prevent the diffusion or migration of these reagents into the pit interiors.

May[35] has proposed a chemical screening mechanism at pit sites on a copper surface to account for their stability. He believed that the cuprous ions released at the pit anode rapidly diffuse outward and react with dissolved oxygen, thereby preventing its diffusion into the pit interior. Colgate[60] has utilized a similar mechanism to explain oxygen screening at pit sites on stainless steels. According to this mechanism, ferrous ions within corrosion pits react with oxygen and prevent it from repassivating the pit anode. Although these mechanisms may contribute to the stability of corrosion pits, they are only applicable to a limited number of cases. These mechanisms explain only oxygen screening, and only for metals which release oxidizable metal cations as corrosion products. They do not explain the screening of other passivating species and cannot be applied to the pitting of metals such as aluminum and nickel.

Standifer[16] has suggested that the high

concentration of corrosion products at the base of a pit greatly reduces the solubility of oxygen and thereby retards the diffusion of oxygen to the anodic sites. Chloride and bromide salts, because of their great solubilities, can strongly suppress oxygen solubility.[61, 62] Again, this screening concept can apply only to oxygen screening; it does not explain the screening of ionic species. Unlike the chemical screening mechanisms, Standifer's concept can be applied to oxygen screening at pit sites on all metals.

There is a possibility that the high chloride ion concentrations within growing pits might produce a migrational block to other anions. The conductivities of highly concentrated solutions[63] indicate that chloride ions possess greater mobilities than any other anions under these conditions. Within pit cavities, the migration of chloride ions might be much greater than other anions and, therefore, prevent or retard these other anions from contacting anodic areas. This hypothesis remains to be tested.

Initiation and Growth Concept

The concept of initiation and growth during pitting corrosion was introduced by Aziz and Godard[64] in 1952. The authors stated that "Experience in this laboratory has suggested the conclusion that pitting should be divided into two separate stages—initiation and propagation. In the opinion of the authors the factors affecting the propagation of a pit are different from those that led to its initiation. A pit can be started by artificial stimulation at an otherwise normal site on a metal surface, yet continue to propagate if given the right environmental conditions."

The concept of pit initiation and pit growth has since been widely used to explain pitting corrosion phenomena.[4, 35, 53]

Although the term pit initiation has been frequently used, it has never been really defined. This point has been discussed previously by Greene.[65] The following list of implied (but not defined) meanings is used by various investigators in describing the term pit initiation:

1. A separate, unspecified process, distinct from pit growth

2. The probability of pitting attack

3. The number of pits appearing on a metal surface after the application of an anodic current

4. The early erratic stages of pit growth

5. The destruction of the passive surface state of a metal

6. The incubation period prior to the appearance of visible pits on an exposed metal surface

7. A term synonymous with pitting corrosion

From the above, pit initiation is obviously a vague and an almost all-inclusive term. There is a pressing urgency to define this term. Used in its present form, it can only confuse the understanding of pitting phenomena.

Study Methods

The localized and random character of pitting corrosion makes it difficult to devise suitable techniques to measure and observe this phenomenon. The following sections describe the various methods which have been applied to the study of pitting attack.

Visual Observations

Visual observations of the pitting process and pitted metal surfaces have yielded much useful information about the loci and forms of pits and the distribution of corrosion products. The use of electron microscopy[15] and radiographic techniques[66] has increased the scope of visual observations. A major disadvantage of this type of observation is its qualitative nature. Such observations are difficult to compare or correlate.

Quantitative Measures of Attack

Both practical and fundamental studies of pitting corrosion are hampered by the difficulty in choosing a suitable way of quantitatively measuring and comparing the extent of corrosive attack. Ordinary weight loss determinations and calculated overall corrosion rates do not reflect the localized character of pitting corrosion and are practically useless for comparison purposes.[67, 68] Smith[69] devised a pitting resistance test for stainless steels based on weight loss determinations in a hot, circulating ferric chloride solution. Although the results of this test are reproducible, they cannot be used to predict pitting resistances in solutions other than the test solution because of the reasons stated above. From a fundamental standpoint, the greatest drawback to weight loss determinations is that they indicate only total pitting attack and cannot be used to study the progress of isolated pits.

Both average and maximum pit depths have been utilized in attempts to measure quantitatively the extent of pitting corrosion. Corrosion pits vary widely in intensity and in depth. For this reason, average pit depth is not a desirable way to measure or compare pitting attack. Specimens having identical average pit depths could have widely varying maximum pit depths. At first glance it seems that maximum rather than average pit depth would be a more indicative measurement. However, Evans[70] has pointed out that the magnitude of the maximum pit depth is meaningless unless the specimen size is also considered. The maximum depth of pitting is a function of exposed area; it increases as area increases. Aziz[22] and Eldredge[23] have shown that this problem can be circumvented by the application of extreme value statistics to maximum pit depth measurements.

Potential Studies

The time-potential behavior of a metal in a corrosive electrolyte has been used extensively in the study of corrosion phenomena by investigators too numerous to mention. The potential of a corroding metal yields only one piece of information—the corrosion potential. The usefulness of such measurements is dependent

on how much is known about the anodic and cathodic reactions that occur. Although early workers placed much faith in potential measurements, measurements of this sort have little inherent value by themselves. In fact, corrosion potential measurements can be very misleading. For example, Mears and Brown[71] have shown that potential measurements erroneously indicate that ferric chloride additions inhibit the attack of stainless steel in sodium chloride solutions. Mears and Brown[71] and Standifer[16] have also shown that potential measurements are relatively insensitive to the presence of pits on a metal surface. This can be attributed to the small size of pits relative to the total area of a metal specimen.

Impressed Current Studies

In the realm of pitting corrosion, perhaps the best known impressed current technique is the break-through potential test developed by Brennert[72] and later used by Mahla and Nielsen[73] to evaluate and study the pitting resistance of stainless steels. This test is performed by impressing a continuously increasing potential between a stainless steel anode and an inert cathode and by measuring the current flow and electrode potential of the stainless steel electrode. As the impressed potential is increased, the current flow and the electrode potential also increase. Finally, a point is reached at which there is a sudden increase in current. The electrode potential at this point is called the break-through potential and is believed to result from the rupture of the passive film at localized points on the electrode surface. Mahla and Nielsen demonstrated that there was a fair correlation between the results of this test and pitting corrosion tests in ferric chloride and bromide. Alloys with the greatest break-through potentials generally showed the greatest resistance to pitting attack. However, the results of the break-through potential test lack fundamental significance. Uhlig[74] has shown that measured break-through potentials are related to the decomposition potentials of the electrolytes used in the test. Aziz[75] has criticized this technique from a fundamental standpoint because of the complexities which are introduced and also the authors' contention that the break-through potential is an indication of surface film rupture.

Recently, Streicher[4] has modified the break-through potential test and has developed a pit initiation test. In this test, an increasing potential is applied between a standard size stainless steel anode and an inert cathode. The potential is increased to two volts and held at this value for five minutes. Then, the number of pits appearing on the stainless alloy specimen is counted. According to the author, the number of pits observed is a measure of the pit initiation tendency of the stainless steel specimen. Like the break-through potential test, the results of this test are not easily applied to an explanation of pitting corrosion mechanisms. The test does not duplicate the conditions present during actual pitting corrosion.

Impressed currents through divided cells have been used by Uhlig[6] and Pryor[31] to study ion migration and pH changes occurring in pitting corrosion.

Artificial Pits

Instead of attempting to observe and measure the pitting of a metal surface with all the inherent difficulties that this entails, an artificial cell or artificial pit that duplicates the conditions during pitting can be constructed and operated. Mears and Brown have made extensive use of artificial pits in their pitting corrosion studies. Their first artificial pits were constructed from pitted metal specimens.[75] This was accomplished by coupling two previously pitted panels, one completely waxed except for the pitted areas, the other waxed only on the pitted areas. The panels were replaced in the pitting corrosive, and the resulting current flow was measured. These investigators also developed and used the now famous scratch pit technique.[38, 76, 77] This method utilized two metal panels, one completely exposed, the other completely waxed. The waxed panel was scratched in several places to expose the metal. The two panels were coupled, immersed in a suitable corrosive, and the resulting current flow measured. In a later investigation, Brown and Mears[78] developed still another artificial pit design. The pits on an aluminum sheet were removed by making a circular cut around them. They were then replaced in their original positions and insulated from the sheet with wax. Electrical connections were made to the pits and sheet, and the resulting current flows were measured in a corrosive solution. Aziz[79] has also used this technique in a recent pitting study.

Parsons, Cudd, and Lochte[30] developed an artificial pit to study the pitting of iron. Their pit consisted of a fine iron wire sealed into the bottom of a glass tube. This wire was connected, by means of an insulated lead, to a spiral of copper wire at the open end of the tube. The entire assembly then was immersed in a pitting corrosive with the open end of the tube pointing upward. This technique permitted a precise analysis of the composition of the pit interior after various exposure times.

Evans and Davies[80] employed an artificial pit of zinc to demonstrate that corrosion currents flow even in high resistance electrolytes such as distilled water. The pit specimen consisted of a piece of plastic sandwiched between two sheets of zinc. A small hole passed through the upper zinc sheet and through the plastic to the lower sheet. In operation, the external surface of the bottom zinc sheet and the electrical connections to the two sheets were coated with insulating material. In appearance, this pit specimen closely resembled an actual pit.

May[35] has studied the pitting of copper by an artificial pit technique. For this purpose, two electrodes were used: one a bare copper cathode, the other a copper anode contained in a small, open glass compartment. The anode compartment was packed with a mixture having the same composition as the contents of actual corrosion pits.

There are several criticisms of the artificial pit technique. First, most of the artificial pit designs that have been used are not geometrically similar to actual corrosion pits. The notable exceptions are the "cut-out" pits used by Brown and Mears[78] and Aziz[79] and the pit employed by Evans and Davies.[80] As shown by Agar and Hoar[81] and Waber,[82] the size and shape of a cell can strongly influence its electrochemical behavior. Thus, to obtain accurate results from an artificial pit, it is necessary that the pit be almost geometrically identical to an actual pit.

Secondly, local action currents on the electrode of an artificial pit will not be detected during the measurement of current flow between the anode and cathode electrodes. If these local action currents are large enough, they could introduce misleading results. This factor has been suggested by Fink.[83] Finally, the fact is both desirable and undesirable that most artificial pit techniques measure only the behavior of a single pit. It is desirable since the technique isolates one pit and eliminates interference from other pits. However, because of the random behavior of corrosion pits, an artificial pit cannot be considered representative of all corrosion pits. Many artificial pits would have to be constructed and studied before any generalized conclusion could be made about over-all pitting behavior. Artificial pit techniques are most applicable to the study of single rather than many pits.

If constructed and used carefully, artificial pits offer a unique means of studying pitting attack. They permit a closer control and allow a more precise observation of the pitting process than any other study technique.

Indicator Studies

Chemical indicators have been used in numerous corrosion studies to indicate the beginning of corrosion and the distribution of the electrochemical reactions on a metal surface. Ferroxyl indicator is the one most frequently used in studies of iron and ferrous alloy surfaces.[16, 84, 85] However, Bengough and Stuart[86] directed some important and still unanswered criticisms against the ferroxyl technique as early as 1922. The effect of the agar gel on the results obtained with ferroxyl indicator has never been determined. Also, the presence of ferricyanide ions in the indicator could have a marked effect on the electrochemical behavior of a metal surface.

The availability of radioactive isotopes in recent years has permitted the development of a new and powerful research tool—the radiotracer technique. Radioactive tracers have been used by Aziz[87] to determine the distribution of electrochemical reactions during the pitting of aluminum. Simnad and Ruder[88] also have used this technique to study the local action on stainless steel surfaces. This method is based on the principle that Co^{60} or other heavy metal radioisotopes are deposited at cathodic areas by electrochemical action. However, Foley, Stark and Guare[89] have recently shown that there are three proc-

esses by which Co^{60} ions can become associated with metal surfaces: exchange between surface metal atoms and Co^{60} ions in solution, adsorption and electrolytic deposition. Radiotracer indicator techniques require further refinements. Recent developments in high resolution autoradiographic methods[90, 91, 92, 93] could extend the usefulness of these techniques.

Radiotracers have also been used in other studies that are directly related to various aspects of pitting corrosion. Simnad[94] has prepared a summary of these studies.

Additional references on pitting corrosion can be found in the annotated bibliography recently prepared by Benton.[95]

Summary

This analysis has indicated the following important points concerning pitting corrosion:

1. Definitions and terminology used in describing pitting attack are ambiguous in many instances. Pitting corrosion has not been defined or characterized adequately.

2. Pit sites appear to be almost randomly distributed in relation to metal surface structure, with some preference for grain and twin boundaries. Pit sites are not random with respect to each other because of interaction effects.

3. Pitting corrosion behavior can be related to the particular cathodic reaction which occurs during attack. Pitting in systems where oxygen reduction is the major cathodic reaction demonstrates marked differences from attack in systems in which metal ion reduction is the controlling cathodic reaction.

4. The concepts of polarization and electrochemical control will probably have to be modified when applied to pitting corrosion.

5. There are no completely satisfactory theories of pitting corrosion.

6. The application of artificial pit techniques to the study of pitting corrosion has not been exploited completely. Studies of this type should be of great value in the understanding of the pitting corrosion process.

Acknowledgments

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Any discussions of this article not published above will appear in the June, 1959 issue

Part 1—Pit Growth

An Electrochemical Study
Of Pitting Corrosion in Stainless Steels*

By N. D. GREENE and M. G. FONTANA***

Introduction

PURPOSE OF this investigation was the characterization of pit growth in 18 percent chromium-8 percent nickel stainless steels exposed to ferric chloride solutions. The study of pitting corrosion phenomena is inherently difficult because of the randomness, the small size and the varying activities of the corroding sites. Many of these difficulties can be avoided by constructing a cell or artificial pit that closely duplicates the conditions of actual pitting attack. The advantages and limitations of using artificial pit methods to study pitting corrosion have been discussed by the authors.[1] Although artificial pits have been previously used in pitting corrosion studies,[2-9] the design, construction and scope of application of the artificial pits used in this study present a unique experimental approach.

This fundamental study of pitting was instigated by the Alloy Casting Institute.

Experimental

Artificial Pit Specimen

The artificial pit specimen is illustrated in Figure 1. It consisted of two electrically insulated electrodes mounted in cold-setting plastic. The cathode was a thin sheet of stainless steel alloy, one inch square, set in the surface of a plastic mount. A fine wire anode of the same material passed through a small hole in the center of the cathode sheet. The plastic mounting material surrounded the wire and prevented electrical contact with the sheet. Electrical connections to the two electrodes were made by soldered, plastic-coated wires that entered through the base of the specimen.

The specimen mount was approximately 1.5 inches in diameter and 0.5 inch thick. Anode wires varying between 0.005 and 0.031 inch diameter were employed in pit construction. Separation between the two electrodes varied between 0.003 and 0.010 inch maximum for all the standard specimens prepared for this investigation. Most of the specimens had anode-cathode separations of 0.005 inch.

Compared to other artificial pit designs,[2-9] the artificial pit specimen described above is unique in its similarity to actual corrosion pits. The high

cathode/anode area ratio, the planar placement of the electrodes, and the small electrode separation lend to this similarity. As shown by Agar and Hoar[10] and Waber,[11] the size and shape of an electrolytic cell can strongly influence its electrochemical behavior. Thus, to duplicate pitting behavior, an artificial pit must be almost geometrically identical to an actual pit.

Test Cell

The test cell and its component parts are illustrated in Figures 2 and 3. Figure 2 is the test assembly which fits into a wide-mouth, 1000-ml flask, as shown in Figure 3. The pit specimen rested on the Teflon support and was completely immersed in the corrosive solution. The atmosphere and dissolved gas in the solution were controlled by continuously admitting the desired gas through the gas inlet tube. Electrical connection between the pit specimen and the external measuring circuit was made through the stopper. The glass and Teflon construction of the test cell prevented contamination of the electrolyte.

Throughout this study, the following standardized conditions were maintained in the test cell: the cell contained 400 ml of electrolyte during every test run. During all tests, except those so noted, the corrosive was continuously saturated with oxygen entering the inlet tube at 0.5 liter/minute. All tests were conducted at an ambient temperature of 80 ± 2 F.

Electrical Circuit

The electrical circuit is schematically pictured in Figure 4. The actual circuit consisted of four circuits similar to Figure 4, with a switching arrangement for connecting the potentiometer into any one of them. This permitted simultaneous measurement and control of more than one pitting system. Current was controlled by voltage dividing across a series of variable resistors. A precision potentiometer was used to measure current flow and the potential difference between the pit specimen electrodes.

The electrical circuit provided very versatile operations and accurate measurement and control of impressed currents. With a zero potential difference maintained between the pit specimen terminals, the circuit also functioned as a zero-resistance ammeter.

Abstract

By means of a unique artificial pit specimen, pit growth on 18 percent chromium-8 percent nickel stainless steel has been measured and characterized. The effects of solution composition, agitation, atmosphere, corrosion current interruption, chloride ion concentration, and inhibitor additions have been investigated. Pit interaction during pit growth has also been determined. The autocatalytic nature of pitting has been verified, and evidence of ion screening at pit sites has been experimentally observed for the first time. 3.2.2

Materials

The materials used in this study are listed in Table 1. All the pit specimens were constructed from the as-received sheet and wire because trial tests indicated no observable difference between pits prepared from as-received material and those consisting of material solution quenched from 2050 F. All electrolytes investigated were prepared from reagent-grade chemicals and double-distilled water. Exceptions to this were ferric bromide and ferric perchlorate, which were prepared by dissolving precipitated ferric hydroxide in the corresponding acid. For this reason, the reported concentrations of these two solutions are inaccurate. The pH values of all the electrolytes studied varied between 1.5 and 2.5. Exploratory tests indicated that pH values within this range produced no noticeable effect on the behavior of the pit specimens.

Results and Discussion

Open-Circuit Behavior

The open-circuit potential differences of Type 304 stainless steel pit specimens were measured in 0.1 molar solutions of ferric bromide, ferric chloride, ferric perchlorate, ferric sulfate, sodium bromide, sodium chloride and sodium nitrate. In every instance, the wire became anodic after the passage of sufficient time. These open-circuit potential differences were not reproducible for a given specimen and solution. Also, no trends or correlations were found between the observed potential differences and the solutions studied.

The anodic behavior of the wire electrode during open-circuit conditions is an example of the area/perimeter ratio effect first observed by Francis and co-workers.[12] They observed that an 18-8 stainless steel panel with a waxed grid painted on its surface always was anodic with respect to a bare panel when immersed in ferric chloride. When the panels were coupled,

Figure 1—Artificial pit specimen. The cathode is a thin sheet of stainless steel one-inch square.
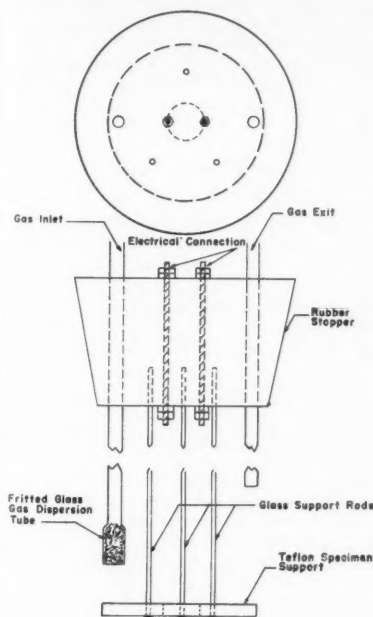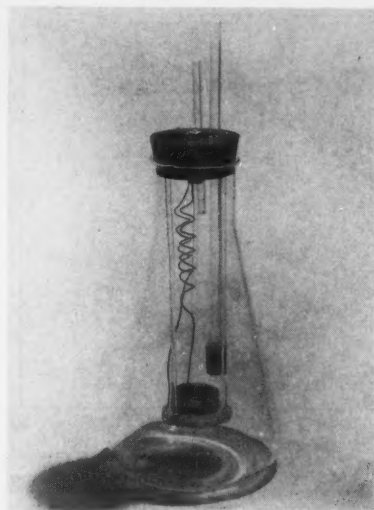
Figure 3—Flask to hold test assembly.

Figure 4—Circuit diagram for artificial pit studies.

Figure 2—Test assembly.

the current flow between them was observed to be proportional to the relative area/perimeter ratio of the waxed specimen. These investigators postulated that this behavior was caused by the crevice corrosion occurring at the wax-metal interfaces. Hence, an area with a large edge length will contain a greater proportion of anodic sites than an identical area with a shorter edge length. Considering the artificial pit specimens, it is apparent that the wire had a very small area/perimeter ratio compared to the sheet, and, therefore, was more anodic.

Pit Activation

When artificial pit specimens of Type 304 stainless steel were short-circuited and immersed in ferric chloride solution, they usually became active and began generating current. However, some of the specimens remained inert under these conditions, and several techniques were used to activate them. These techniques were based on the idea of producing those conditions which are present during pit growth—namely, high chloride ion concentration and low pH values at the pit anode.

The usual method of activation was the application of an impressed current (wire anodic). Currents between 10 and 60 microamperes were applied for periods

up to five minutes, after which the specimens usually became self-sustaining and generated their own current. Higher impressed currents were not so effective in actuating inert pit specimens.

More drastic measures were used to activate pits which were not stimulated by the above method. One technique consisted of placing a drop of concentrated hydrochloric acid on the anode wire of a specimen immersed in ferric chloride solution. Also, inert specimens were often stimulated by starting them in a very severe pitting corrosive, such as concentrated ferric chloride, and then transferring them to the solution under study. This is the transfer technique which is described in a later section.

The artificial pits showed erratic activation tendencies. Some became active immediately after immersion; several remained inactive even after the anode wire had been almost dissolved by various stimulation attempts. Also, a given specimen usually showed a variable activation behavior in identical experiments. In general, previously used specimens were more readily activated than unused specimens. Likewise, ease of activation increased with increasing ferric chloride concentrations.

Although a pit specimen was considered inactive, a current flow was generally observed. This current was small, usually 0.1 microampere or less. Such currents were observed even for specimens immersed in non-pitting electrolytes such as ferric sulfate and sodium nitrate. These small currents are a result of the area/perimeter effect between the wire and the sheet. Thus, during artificial pit studies, the area/perimeter ratio effect tends to exaggerate the pitting tendencies of the solutions under study.

TABLE 1—Composition of Materials

Stainless Steel Alloy Type	Form (inches)	PERCENT COMPOSITION								
		Cr	Ni	C	Mn	Si	S	P	Mo	Cu
304	0.005 wire	18.68	9.75	0.060	1.21	0.45	0.029	0.027	....	....
304	0.010 wire	18.72	9.03	0.071	1.60	0.48	0.014	0.020	....	....
304	0.020 wire	18.55	9.30	0.070	1.20	0.56	0.030	0.029	0.10	0.22
304	0.031 wire	18.85	9.44	0.050	0.72	0.66	0.020	0.026	....	0.37
304	0.005 sheet	18.74	8.88	0.10	1.46	0.49	0.018	0.028	....	....
316	0.010 wire	17.33	13.08	0.039	1.67	0.45	0.023	0.023	2.39	....
316	0.030 sheet[1]	16–18[2]	10–14	0.10 max.	....	....	.....	.....	2–3	....

[1] Nominal Composition.
[2] Cold-rolled to 0.011 inch prior to use in artificial pits.
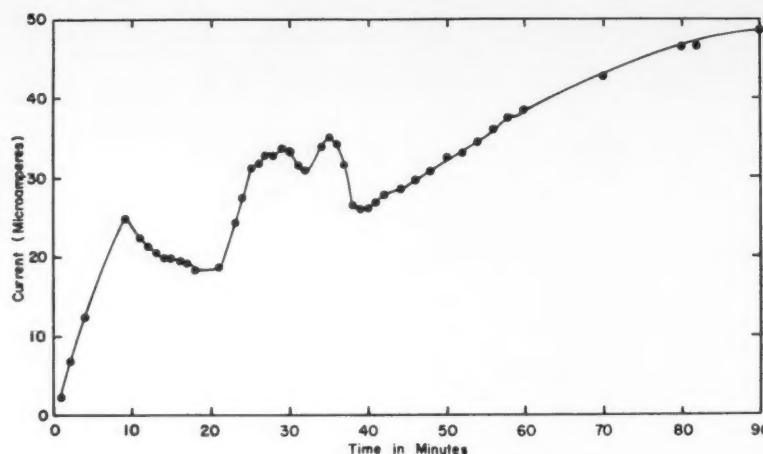
Figure 5—Growth of an artificial pit in 0.1 M FeCl₃ + 0.08 N HCl. Cathode area is 1.0 sq. in. Anode wire is 20-mil diameter.

Figure 6—Current decay of an artificial pit during open circuit conditions. Points are instantaneous readings. Cathode area is 1.0 sq. in. Anode wire is 20-mil diameter.

Pit Growth Characteristics

The growth of a Type 304 stainless steel pit specimen in 0.1 molar ferric chloride is shown in Figure 5. The current shown is the self-generated, short-circuit current and is directly related to the corrosion rate of the anode electrode. Pit growth is characterized by a very erratic corrosion or growth rate during the early stages of pit development. Many of the artificial pits tested suddenly lost their activity during this early growth period. This initial instability of corrosion pits has been observed by other investigators[8, 13, 14] and is an indication of the autocatalytic nature of the pitting process. The stability of the artificial pits increased with time, and the loss of pit activity during the later growth stages was rarely observed.

Pit growth is characterized by a rapid increase in corrosion rate with time. The pit specimen illustrated in Figure 5 shows a 25-fold increase in corrosion rate during its first 90 minutes of growth. No limiting corrosion rate was observed; even in three-hour tests the rate continued to increase slowly. It was not possible to appreciably accelerate the corrosion rate of a pit specimen by impressed currents. Although some stimulation was possible, high corrosion rates were achieved only by allowing the pit to remain short-circuited for long periods. In many instances, the application of even small currents to a growing pit reduced its corrosion current value. This inability to speed up the pitting process in artificial pits has also been reported by May.[8] Apparently, the reactions within a pit are extremely critical, and the conditions leading to increased pit activity are time-dependent and cannot be hastened by external means.

It is important to emphasize that Figure 5 is not representative of all pit specimens tested in 0.1 molar ferric chloride. Pit growth characteristics were not reproducible in identical tests even using the same specimen. Several specimens refused to become self-sustaining under any conditions. Some became inactive after a short growth period; others showed ex-

tremely rapid increases in corrosion rate with time. The magnitude and duration of the initial corrosion current fluctuations varied from specimen to specimen and also during identical tests with the same specimen. However, Figure 5 does illustrate qualitatively the growth behavior of most active pits—namely, an erratic and unstable incubation period followed by a period of increasing pit activity.

The highly variable behavior of the artificial pit specimens closely corresponds to the observed behaviors of actual corrosion pits. Hence, it is an indication of their similarity to real corrosion pits. May[8] has observed similar non-reproducibility in his experiments with artificial pits of copper immersed in water and dilute salt solutions.

The wire surface was not attacked uniformly during pitting studies but showed numerous localized pits. Also, edge attack was frequently observed along the wire-plastic interface. The localized attack of the wire suggested that local corrosion currents may have occurred on the wire surface, the unattacked areas of the wire acting as cathodic areas. This idea was supported by measurements described elsewhere.[15] However, the magnitude of these local currents was small compared to the measured corrosion currents. This was illustrated by the fact that open-circuited pit specimens showed no visible attack of the anode wires nor any enlargement of existing pits when exposed to 0.1 and 0.2 molar ferric chloride solutions for periods up to 24 hours. Thus, the measured corrosion current corresponded closely to the total corrosion current.

Although the wire electrode was observed to contain numerous pits, it can be considered as a single pit since actual pit cavities have been shown to contain cathodic as well as anodic areas.[8, 16, 17] Defining the pit to include some cathodic areas is a necessity in all artificial pit techniques.

The corrosive solutions were chosen so that no pitting occurred on the cathode sheet during normal test runs (up to 3
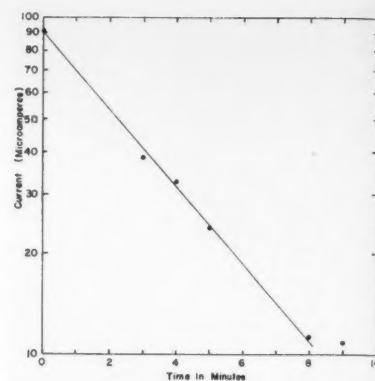
hours). However, with longer exposures, all of the pitting corrosives produced pitting and edge attack of the cathode electrode.

Several estimates were made of the anodic and cathodic current densities during attack in 0.2 molar ferric chloride. Cathodic current densities ranged from 10 to 100 microamperes/square inch while anodic values ranged from 1 to 10 amperes/square inch. The high anodic current explains the extremely rapid pit penetration observed in ferric chloride solutions.

Factors Affecting Pit Growth

Anode Wire Diameter

Type 304 stainless steel pit specimens with wire diameters of 0.005, 0.010, 0.020 and 0.031 inch were tested in ferric chloride. Because of the localized attack of the anode wire, the diameter of the wire had no effect on the pit growth characteristics. The 0.005- and 0.010-inch wires were difficult to mount and were often destructively undermined during corrosion attack. Pits with 0.020 inch anodes were considered the most desirable since they were easy to assemble, and were not usually undermined during testing which allowed them to be reused. From the standpoint of geometric similarity to actual pits, the 0.020-inch anode was more desirable than the 0.031-inch anode.

Agitation

Agitation of the ferric chloride solutions slightly increased the activity of growing pits. This increase was often only momentary. Even violent shaking of the test cell failed to cause any appreciable reduction in the activities of stable, growing pits. Agitation apparently increased the supply of ferric ions at the cathode electrode and did not disturb the autocatalytic conditions existing at the pit anode.

Atmosphere

The atmosphere within the test cell produced no observable effect on the pitting tendencies of ferric chloride solutions. The substitution of nitrogen for the usual oxygen atmosphere did not affect pit growth characteristics. From previous study concerning the effect of
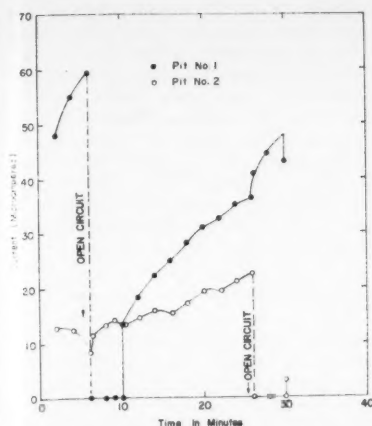
Figure 7—Pit interaction during growth in 0.2 M FeCl₃ + 0.5N HCl. Cathode area is 0.005 sq. in. Anode wire is 20-mil diameter. Anode separation is 0.038 in., center to center.
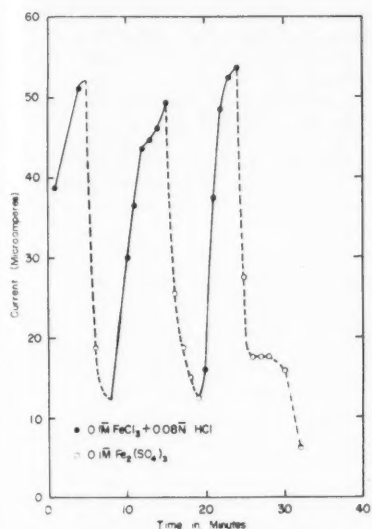
Figure 8—Transfer studies in ferric sulfate. Cathode area is 1.0 sq. in. Anode wire is 31-mil diameter.

Figure 9—Transfer studies in ferric perchlorate. Cathode area is 1.0 sq. in. Anode wire is 10-mil diameter.

oxygen on the corrosivity of oxidizing metal halides,[1] this is the expected result. The cathodic reduction of oxygen is a minor reaction during pitting in ferric chloride. Stagnant solutions showed a slightly slower increase in pit activity than solutions with gas bubbling through them. This was undoubtedly due to the stirring effect of the gas bubbles rather than any specific chemical action. Oxygen was used as the standard test atmosphere to keep test conditions identical and to retard any build-up of ferrous ions during long test runs.

Current Interruption

Figure 6 illustrates the effect of current interruptions on the activity of an artificial pit immersed in 0.1 molar ferric chloride. The points were obtained by opening the circuit of an active pit specimen and making rapid short-circuit current measurements at various time intervals. Each current determination took 5 seconds or less to perform. The duration of the measurements was considered so

short that no increase in pit activity occurred during the measurements. Thus, the curve represents the activity that a pit specimen, originally at 90 microamperes, would have after being interrupted for various time periods. Even momentary current interruptions produced marked decreases in pit activity. Figure 6 is probably the first direct experimental evidence of the autocatalytic nature of pitting corrosion.

The apparent logarithmic relationship shown in Figure 6 suggests the phenomena of non-steady-state diffusion. The general equation of the current decay curve in Figure 6 is

$$\text{Log } I = -Kt + k \qquad (1)$$

where I is current flow at time t; K and k are constants. The diffusion of the concentrated pit contents into the bulk solution during open-circuit conditions will be closely approximated by a general expression for non-steady-state diffusions:

$$\frac{dC}{dt} = -K'C \qquad (2)$$

or

$$\log C = -K''t + k' \qquad (3)$$

where C is the concentration of the chloride ions within the pit at time t; K', K'' and k' are constants. Thus, pit activity or pit current appears to be directly related to the concentration or amount of chloride ion within the pit.

The decay of the anode and cathode potential difference during open circuit was also determined. The potential decay was observed to be much slower than the current decay. For example, a pit specimen in 0.1 molar ferric chloride with an initial open-circuit potential difference of 0.339 volt dropped to 0.200 volt after 12 minutes. It was not possible to determine whether potential decay was a logarithmic function because of the short range of potential values. The area/perimeter ef-

fect prevented accurate determinations at low potential differences. The slow decrease in potential difference compared to the rapid decrease in corrosion current suggests that the current decay was due mainly to a shrinkage of the anodic area within pits caused by a reduction in chloride ion concentration. Changes in anode area are discussed further elsewhere.[15]

Pit Interaction

Possible interaction effects between pit sites were studied with double artificial pit specimens containing two 0.020-inch anode wires separated by distances of 0.165, 0.070 and 0.038 inch, center to center. These were tested in 0.2 molar ferric chloride. Several techniques were employed to detect pit interaction effects. The first consisted of activating one of the pits and observing its short-circuit current while an anodic current of 100 microamperes or more was impressed through the other anode wire. In the second method, both pits were activated, and their short-circuit current behaviors were observed to determine if there was any relationship between the activities of the pits. In the third technique, the two pits were stimulated to active growth and the short-circuit behavior of one was watched while the other was inactivated by opening its circuit.

No detectable interactions were observed during tests on the three double pit specimens. However, reduction of the cathode electrode size by masking with insulating enamel produced marked interaction effects. The reduction of the cathode size of an artificial pit specimen is equivalent to the existence of numerous corrosion pits on the cathode sheet. It is similar in that it increases the cathode current density and causes greater cathodic polarization than would the exist-
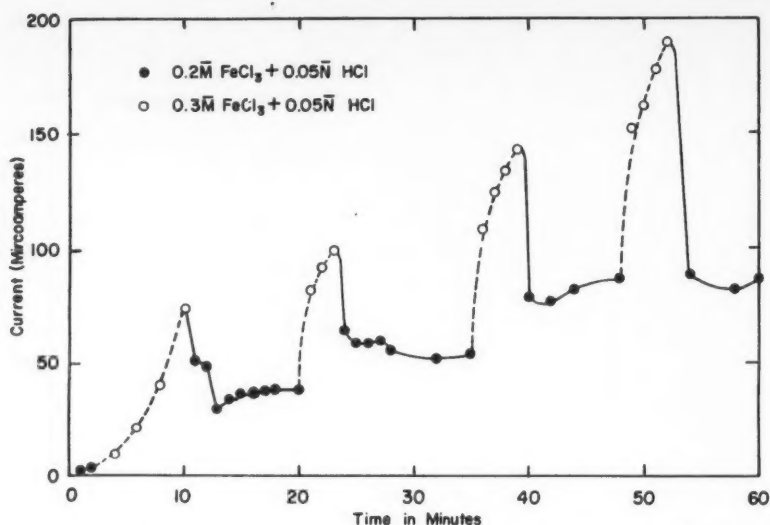
Figure 10—Transfer studies in ferric chloride. Cathode area is 1.0 sq. in. Anode wire is 31-mil. diameter.
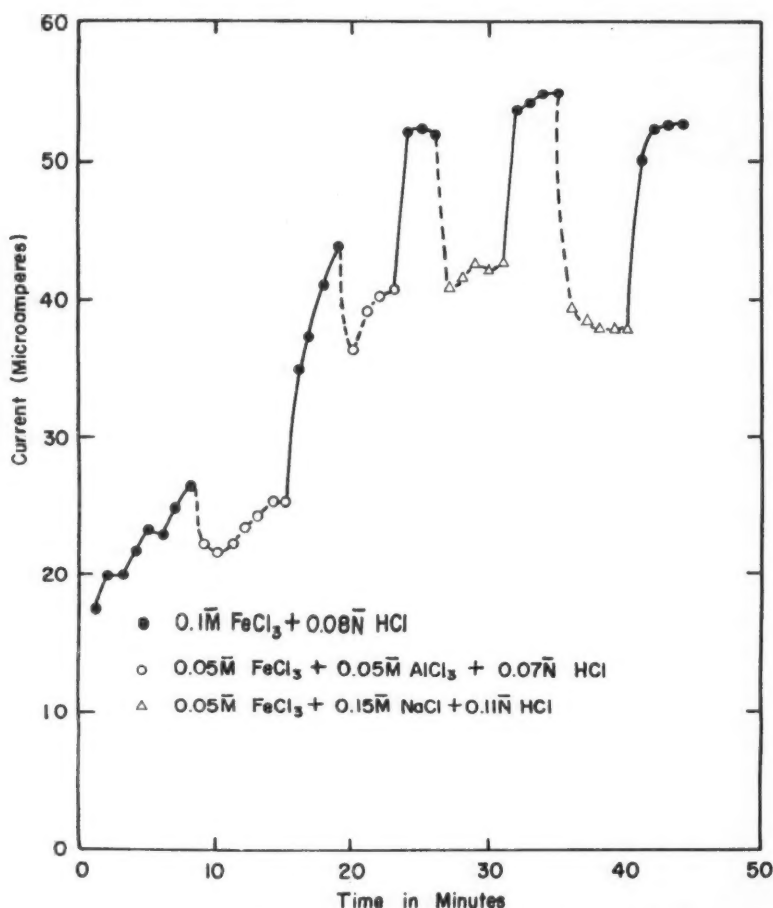
Figure 11—Transfer studies in chloride salt mixtures. Cathode area is 1.0 sq. in. Anode wire is 20-mil diameter.

ence of numerous pits. Figure 7 illustrates the observed interaction on a double pit specimen with a reduced cathode electrode size. The cathode area measured 0.099 by 0.055 inch.

When the circuit of one pit was opened,

the activity of the other increased. Likewise, closing the circuit of a pit reduced the activity of the other. This effect was most noticeable during the inactivation and activation of pit number 2. These observations suggest the following hy-

pothesis: in ferric chloride, and possibly other high conductivity pitting corrosives, there is negligible interaction between two closely spaced, isolated pit sites. Pit interactions apparently occur only on densely pitted surfaces. This concept not only represents a departure from the idea that a single pit suppresses attack in its immediate vicinity[16, 18] but also explains the frequently anomalous observation of two or more corrosion pits in extremely close proximity.[19]

Other Growth Studies

Exploratory experiments were performed with Type 304 stainless steel specimens exposed to 0.1 molar ferric bromide and cupric chloride solutions. Both of these electrolytes demonstrated pit growth tendencies similar to that of ferric chloride. Intense corrosion currents that increased rapidly with time were observed. Pit growth in cupric chloride was characterized by a steady increase in corrosion current with time. Unlike ferric chloride, cupric chloride produced only small current fluctuations during early growth stages.

Tests with Type 316 stainless pit specimens demonstrated that ferric chloride solutions up to 0.3 molar would not sustain any pitting corrosion. The open-circuit potential differences of these specimens were close to zero.

Transfer Studies

The Transfer Technique

Because of the inherent non-reproducibility of pit growth behavior, the relative pitting tendencies of various electrolytes could not be measured by duplicate tests. However, this difficulty was avoided by transferring an actively growing pit specimen from one corrosive medium to another and by observing any resulting change in current intensity. The pit specimens were transferred by moving the entire test assembly, shown in Figure 2, from one test cell to another. During the transfer, electrical connections were maintained. Also, the test assembly was always held so that a layer of electrolyte remained on the surface of the pit specimen during the operation. Such pit transfers usually took no more than 5 seconds. Tests in which a pit was transferred between two identical solutions demonstrated that a careful transfer operation caused no change in pit activity. In all of the experiments conducted, the transfer operation was repeated several times to ensure that the observed effects were qualitatively reproducible.

Effect of Sulfate Ion

Figure 8 shows the relative pitting tendencies of ferric chloride and ferric sulfate. The change from a solid to a dashed line indicates the transference of the pit specimen from the chloride to the sulfate solution. As shown by the last transfer to the sulfate solution, the pit current rapidly fell toward zero. However, interference from the area/perimeter ratio effect prevented it from actually reaching zero current. The presence of chloride ion is essential to pit activity,

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as proved in Figure 9. The sulfate ion shows no pitting tendency. This non-pitting nature of ferric sulfate has been shown by Stern[20] and Uhlig.[21]

Effect of Perchlorate Ion

The pitting tendency of ferric perchlorate is demonstrated in Figure 9. Like sulfate, perchlorate shows no pitting tendencies. The interference from the area/perimeter effect at the end of the fourth transfer to the perchlorate solution should be noted. The corrosion current leveled off. The observed inertness of ferric perchlorate does not agree with the acid theory of pitting or Hoar's pitting experiments with iron.[22, 23] Ferric perchlorate should have a pitting tendency similar to that of ferric chloride, according to the acid theory. Thus, the high acidity within a pit is probably an effect rather than the cause of pitting attack.

Effect of Ferric Chloride Concentration

Figure 10 illustrates the effect of ferric chloride concentration on pit activity. Increasing the concentration markedly increased pit activity. The first transfer to the 0.3 molar ferric chloride illustrates one of the activation techniques described under *Pit Activation*. The specimen, initially at a very low activity level, was stimulated to a higher activity by transferring to the 0.3 molar solutions for a short period. Additional transfers further increased the pit activity in the 0.2 molar solution.

Effect of Ferric Ion Concentration

During pitting in ferric chloride, both the anion and cation are involved in the corrosion process. The chloride ion is essential to the autocatalytic anodic process as already shown by the transfer studies in sulfate and perchlorate solutions, and the pronounced effect of current interruptions. Likewise, the ferric ion is consumed in the cathodic reduction reaction. This introduces the question of which ion is more important to the overall pitting process.

The effect of ferric ion concentration on pit activity was determined by transferring between pure chloride and chloride salt mixtures containing only one half as much ferric ion. The results of these transfers are pictured in Figure 11. The mixtures contained only 0.05 equivalent of ferric ion per liter compared to 0.1 per liter for the pure solution. The chloride ion concentration was almost identical in all three solutions, 0.4 equivalent per liter. Sodium and aluminum cations cannot be cathodically reduced and, therefore, have no effect on the pitting process. It can be seen from Figure 11 that reduction of the ferric ion concentration noticeably reduced the pit specimen activity. Hence, pitting attack in ferric chloride is controlled to a large extent by the concentration of ferric ion. The accelerating influence of ferric ion on pitting attack has also been observed by Brown and Mears[3] and Benson, Brown and Mears.[4]
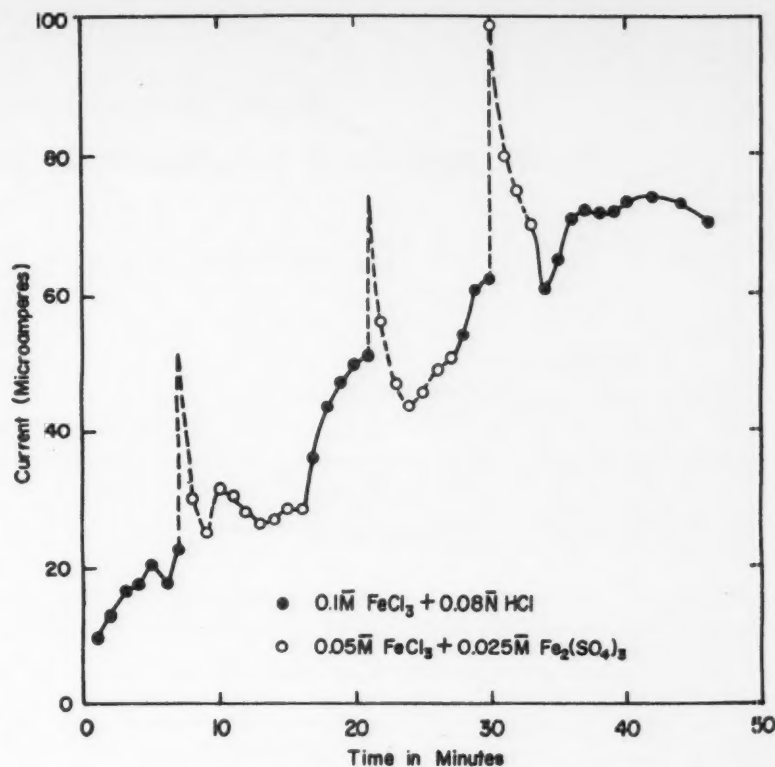
Figure 12—Transfer studies in a ferric chloride-sulfate mixture. Cathode area is 1.0 sq. in. Anode diameter is 20 mils.

Legend in figure:
● 0.1 $\bar{M}$ FeCl$_3$ + 0.08 $\bar{N}$ HCl
○ 0.05 $\bar{M}$ FeCl$_3$ + 0.025 $\bar{M}$ Fe$_2$(SO$_4$)$_3$

Effect of Chloride Ion Concentration

The effect of chloride ion concentration was investigated by transferring between pure ferric chloride and ferric salt mixtures containing only one half as much chloride ion. Figure 12 shows the effect of transferring into a ferric chloride-sulfate mixture. Most unusual is the tremendous burst in pit activity following the transfer to the chloride-sulfate mixture. This behavior is discussed later. In general, after the initial burst in pit activity subsided, the chloride-sulfate mixture showed little effect on pit activity. Thus, the concentration of the chloride ion on the bulk solution had little effect on pitting intensity. Indeed, from the open-circuit current decay behavior it appears that the chloride ion concentration at the pit anode is the controlling factor rather than the concentration in the bulk solution. Of course, the bulk solution composition will exert some influence on the anode chloride concentration. This is evidenced by the results of the transfer studies in ferric sulfate and perchlorate solutions. Evidently, the pit anode requires a continuous supply of chloride from the surrounding solution to offset the loss of chloride by diffusion.

The effect of chloride ion concentration was also studied by transferring between 0.2 molar ferric chloride and a solution containing 0.1 molar ferric chloride and 0.1 molar ferric perchlorate. However, the pit specimen lost all activity in this mixture. An effect similar to Figure 9 was obtained. Apparently,

the perchlorate ion possesses a greater inhibiting power than the sulfate ion.

Effect of Nitrate Additions

The effect of nitrate additions on pit activity is shown in Figure 13. Concentrations of sodium nitrate up to 0.5 molar stimulated the activity of growing pit specimens. A concentration of 1.0 molar first stimulated and then destroyed pit activity. These results are most unusual considering that nitrate has been shown to be a powerful pitting corrosion inhibitor in ferric chloride.[21]

It was impossible to activate pit specimens in 0.1 molar ferric chloride containing 0.05 molar or more of sodium nitrate. Also, when growing pits were open-circuited in nitrate-inhibited ferric chloride until their activities dropped to the vicinity of zero, they could not be reactivated by impressed currents. Although artificial pit tests were not made at nitrate concentrations below 0.05 molar, corrosion tests with the stainless steel sheet immersed in 0.1 molar ferric chloride indicated that a nitrate concentration of 0.018 molar was sufficient to prevent pitting attack during a four-day exposure. Figure 14 shows that a stable, growing pit was not retarded when exposed to ferric chloride containing 25 times this amount of nitrate.

Nitrate inhibits pitting corrosion only when it is present prior to, or possibly during the early stages of, pit growth. Nitrate ion stimulates growing pits except when present in high concentrations.
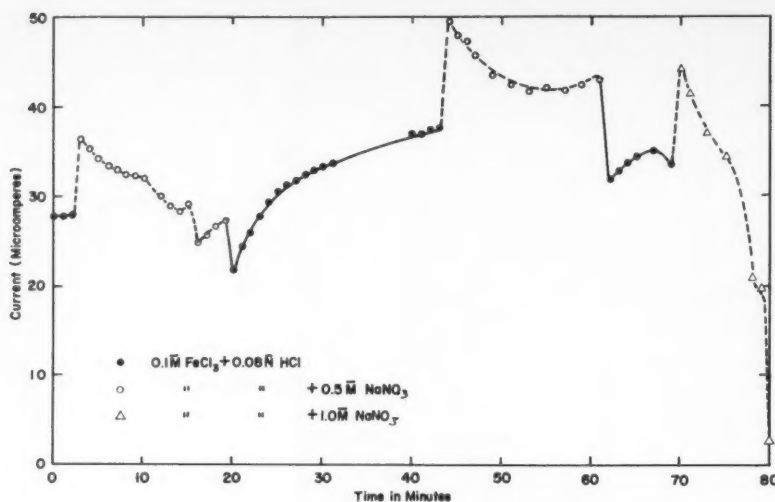
Figure 13—Transfer studies in ferric chloride-sodium nitrate mixtures. Cathode area is 1.0 sq. in. Anode wire diameter is 10 mils.

Ion Screening

Nitrate ion does not affect the cathodic reduction of ferric ion[20] and, therefore, the inhibiting influence of this ion must be due to its effect on the anodic reactions occurring during pitting. If Figure 14 and the activation studies described above are considered, it is probable that nitrate ion concentrations that retard the anodic reactions during pit activation do not suppress the anodic reactions during pit growth. Thus, the nitrate ions must not contact the anodic reaction sites during pit growth except at very high concentrations. The contents of an actively growing pit in some way screen or prevent nitrate ions from inhibiting the anodic reactions that are occurring. The screening of nitrate ions from pit anode areas is due mainly to chemical action. Nitrate ion is reduced by ferrous ion in acid solution.[24] Thus, nitrate ions are chemically reduced by the contents of growing pits and are prevented from migrating to active anodic areas. Migrational ion screening, as postulated by the authors[1] may also contribute to the screening of nitrate ions.

The transfer and activation studies described above represent the first experimental indication of screening effects during pitting attack.

Pit Inertia and Pit Memory

Two unusual characteristics of pitting corrosion should be mentioned. The first is pit inertia: during rapid increases or decreases in corrosion current, the current tended to overshoot its final value. This behavior was often observed after pit transfers. Figures 11, 12, 13, and 14 illustrate this effect during increases and decreases in pit current. Pit inertia was also observed during the early erratic stages of pit growth. This unusual behavior is due to the disturbance of the migration-diffusion balance within corrosion pits.

Pit memory is illustrated in Figures 9 and 10. The most interesting feature of

these curves is the rapid increase in corrosion current following transfers to the ferric chloride solution. The increase was much faster than that obtained during any pit growth studies and showed no evidence of early erratic behavior. The pits appeared to remember their original activity and returned immediately to it. Figure 10 shows that this effect is similar to actual memory phenomena. Thus, the longer the pit remained in the inactive solution, the slower it returned to its original value. The ferric chloride curves in Figure 10 decrease in slope with increasing previous exposures to the perchlorate solution. If the pit specimens were allowed to remain in the sulfate or perchlorate solutions for long periods, they were observed usually to be inactive when transferred back to ferric chloride.

Pit memory apparently results from the reactivation of the original pit anode areas. This suggests that the stability of passive surfaces increases with time. Thus, newly passivated areas are more rapidly destroyed, or activated, than old passive areas.

Summary

The important results and conclusions of this investigation are:

1. A new approach to the study of pitting corrosion has been made possible by the development of a unique artificial pit apparatus.

2. Pit growth on 18 percent chromium-8 percent nickel stainless steel in ferric chloride is characterized by an early, erratic stage followed by a period of steadily increasing growth rate. Pit growth is largely controlled by the amount or concentration of chloride ions contained within the pit cavity and the concentration of ferric ions in the corrosive solution.

3. The autocatalytic nature of pitting has been verified experimentally.

4. In ferric chloride, and possibly under high-conductivity pitting corrosives, there is negligible interaction between two

closely spaced, isolated pit sites. Interaction between pit sites only occurs on densely pitted surfaces.

5. Nitrate ion, a pitting inhibitor, only prevents pitting attack when present prior to, or possibly during the early stages of pit growth. Actively growing pits are stimulated by nitrate salt additions, except for large additions which inhibit pit growth.

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An Electrochemical Study
Of Pitting Corrosion in Stainless Steels*

By N. D. GREENE* and M. G. FONTANA**

Introduction

THIS WORK represents a continuation of previous studies[1] concerned with the mechanism of pitting corrosion in 18 percent chromium-8 percent nickel stainless steels exposed to ferric chloride solutions. A critical analysis of the nature of pitting corrosion has been presented.[2]

This fundamental study of pitting was instigated by the Alloy Casting Institute.

Procedure

An apparatus and artificial pit specimens of Type 304 stainless steel similar to those used previously[1] were employed in this investigation. The electrical circuit used previously was modified by the addition of a Beckman Model G pH meter with a saturated calomel reference electrode (Figure 1). This modified circuit served a threefold purpose: (1) It was used to activate inert pit specimens by the application of impressed currents; (2) It functioned as a zero-resistance ammeter when the current controls were adjusted to maintain zero potential difference between the pit specimen terminals; (3) It was used to measure electrode potentials and current intensities during polarization curve determinations.

Considerations of the electrochemistry of pitting corrosion[2] showed that ordinary polarization diagrams could not be used to represent pitting attack. Instead, instantaneous or rapid polarization diagrams were obtained by rapidly introducing external resistance into a short-circuited pit specimen and measuring the corresponding values of electrode potentials and current intensities.

The pitting corrosive used in this study consisted of 0.2 molar ferric chloride stabilized with 0.05 molar hydrochloric acid.

Results

Instantaneous Polarization Curves

An instantaneous polarization diagram of an artificial pit immersed in ferric chloride is shown in Figure 2. The diagram was plotted from measurements of corrosion potential obtained by allowing a short-circuited pit specimen to grow until its activity reached a value of 17 microamperes. Next, arbitrary amounts of external resistance were introduced by unbalancing the zero-resistance ammeter

circuit so that finite potential differences existed between the pit specimen terminals. The corresponding electrode potentials and current intensities were recorded. The open-circuit electrode potentials were obtained by opening the pit specimen circuit. The determination of Figure 2 took less than 30 seconds.

The significance of an instantaneous polarization diagram should be emphasized. It is not a steady-state polarization diagram. If performed fast enough, it represents the polarization characteristics of a system under the conditions that existed during short-circuit operation. Thus, changes in the electrochemical properties of the electrodes and the differences in solution composition at the electrode surfaces during short-circuit current flow are maintained during the polarization measurements. The open-circuit anode potential shown in Figure 2 is not a steady-state open-circuit potential but the instantaneous open-circuit potential. On open circuit, the potential rapidly became less anodic and approached the potential of the cathode sheet. However, the area/perimeter effect imposed by the pit specimen prevented it from actually reaching the cathodic potential.[1]

Because the instantaneous anodic and cathodic polarization curves were observed to be nearly linear, only the corrosion current, corrosion potential and the open-circuit potentials were measured in most of the following experiments. In this manner, the polarization diagrams were determined in 3 seconds or less. These short periods greatly reduced the chance of errors arising from diffusion during the measurements.

All instantaneous polarization diagrams prepared in this investigation are actual corrosion polarization diagrams. They are not impressed current polarization diagrams.

Effect of Time

The polarization diagram in Figure 2 represents only the electrochemical characteristics of a pit at a specific current value. However, the activity or corrosion current of a pit changes remarkably with time as shown by previous growth studies.[1] Hence, the polarization characteristics of a pit must change also with time.

The effect of time on the instantaneous polarization characteristics of a pit speci-

Abstract

The artificial pit technique has been used to study the electrochemistry of the pitting corrosion of 18 percent chromium-8 percent nickel stainless steel in ferric chloride solutions. Pitting corrosion has been observed to be a highly complex, time-dependent phenomenon. The concepts of polarization and electrochemical control must be modified when applied to pitting attack. A new concept of electrochemical action during pitting, based on the mixed potential theory, has been proposed. 3.2.2

men is illustrated in Figure 3. This diagram was obtained by measuring the polarization behavior of a specimen after it had reached a corrosion current indicated by the curves marked by number 1. After the open-circuit potentials were measured, the specimen was short-circuited again and allowed to grow to a greater corrosion current, and the process was repeated. The specimen did not return immediately to its original short-circuit current value after the open-circuit potentials were measured because of current decay during open-circuit conditions.[1] The numbers do not refer to any standard time interval. A standard time interval between tests would be meaningless since the specimen did not grow normally because of the repeated current interruptions during polarization measurements. The numbers merely indicate the change in instantaneous polarization behavior with corrosion current, which increases with time. The cathodic polarization curves for Diagrams 3 to 10 in Figure 3 have been drawn as a single line to avoid a confusing array of lines. The open-circuit cathodic potentials for Diagrams 3 to 10 varied between —0.007 and 0.001 volt; thus the single cathodic curve closely approximates the actual curves.

Figure 3 also demonstrates that the electrochemical behavior of pitting corrosion is most unusual. The open-circuit anodic potential became more anodic with increasing time; the slope of the anodic polarization curves decreased with increasing time. The cathode electrode showed similar but less pronounced changes with time. These changes in electrochemical characteristics with time will be analyzed in a later section. The important point is that pitting corrosion cannot be represented by a single polarization diagram. Since there is an instantaneous polarization diagram for every pit corrosion current value, an infinite number of diagrams are required to illus-
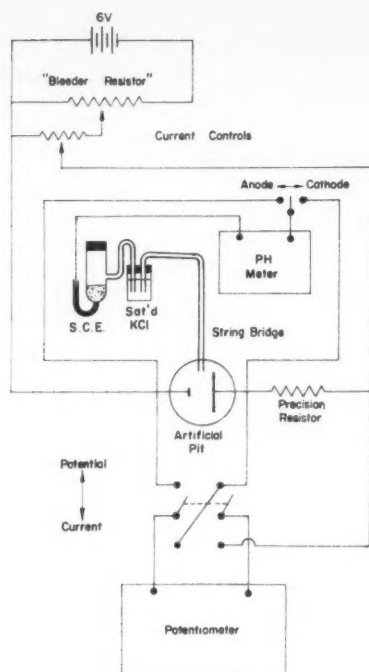
Figure 1—Circuit diagram for artificial pit studies.

Figure 2—Instantaneous polarization curves in $0.2\overline{M}$ $FeCl_3$ + $0.05\overline{N}$ HCl. Cathode area = 1.0 sq. in. Anode wire diameter = 31 mils.

Figure 3—Effect of time on instantaneous polarization cures in $0.2\overline{M}$ $FeCl_3$ + $0.05\overline{N}$ HCl. Cathode area = 1.0 sq. in. Anode wire diameter = 20 mils.
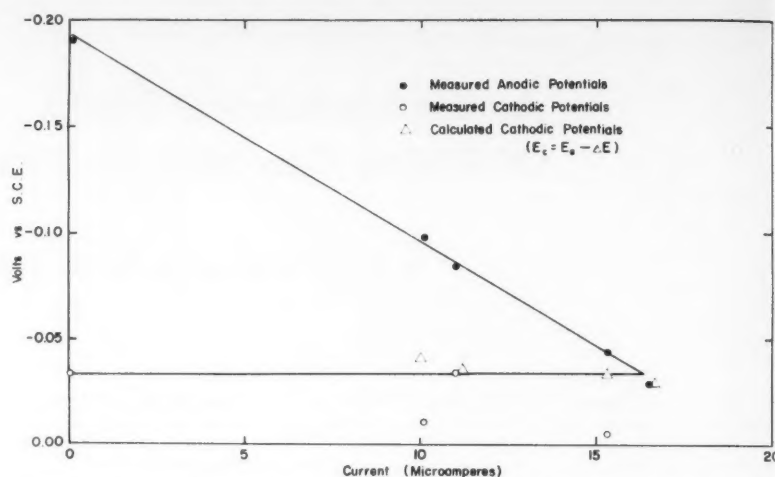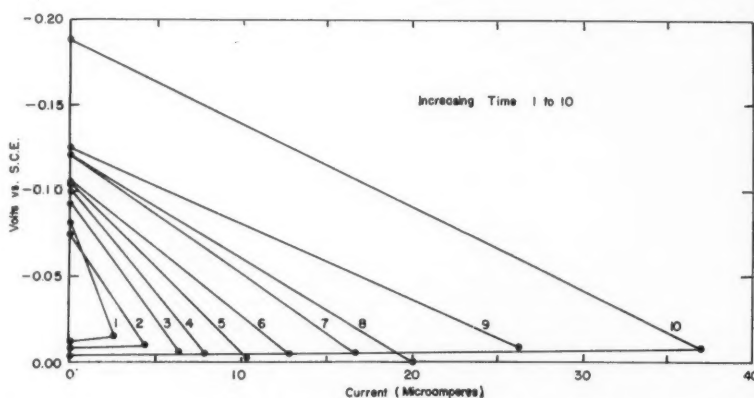

Figure 4—Ef
tion curves
area = 0.25

trate pitting corrosion completely. Corrosion polarization diagrams similar to Figure 3 have been measured also by Brown and Mears[3] by an indirect method.

Effect of Cathode Electrode Area

The cathode electrode areas of the standard pit specimens were altered by masking various amounts of the cathode sheet with insulating enamel. In all cases, the reduced cathode areas were square in shape. From the standpoint of symmetric current distribution, circular cathode areas would have been more desirable. However, the painting of accurate circular areas was difficult. Small, accurate square areas were easier to mask and permitted precise area measurements. All areas were measured with a microscope fitted with a micrometer eyepiece.

Figures 4 through 7 illustrate the effect of cathode electrode area reductions on polarization behavior when compared to Figure 3. Figure 4 illustrates that a fourfold reduction in area produced no observable changes in the polarization curves compare to the 1 square inch electrode. The creeping cathodic polarization curves shown in Figure 4 resulted from the fact that polarization measurements were started before the open-circuit potential of the cathode had stabilized. This phenomenon occurred frequently during the polarization studies. If the cathodic polarization curves of the four diagrams are superimposed, a series of curves similar to Figure 3 result.

Figures 5 and 6 show that further reductions in cathode area produced marked changes in the polarization characteristics of the pit specimens. The instantaneous open-circuit cathodic po-

tential shifted to more noble potentials with increasing time. Also, the slopes of the cathodic polarization curves decreased with time. The symmetric electrochemical behavior of the anode and cathode pictured in Figure 5 is striking. Comparison between Figures 5 and 6 shows that decreasing the cathode area produces an even greater suppression of the open-circuit cathodic potential. Another interesting aspect of these two figures is the relatively constant corrosion potentials.

As the area of the cathode electrode is decreased, its area/perimeter ratio also decreases. At very small cathode areas, interference from this effect was encountered. Figure 7 illustrates this interference. Note that the open-circuit cathodic potential for Diagram 1 is very high in comparison to all the figures previously cited. Also, the suppression of the cathodic open-circuit potential does not follow the trend observed in Figures 3, 4, 5 and 6. Obviously, at a cathodic area of 0.003 square inch, the area/perimeter effect exerted considerable influence on the cathodic behavior. This area/perimeter interference is not serious

because the curves still show the same qualitative polarization characteristics.

The time behavior of the instantaneous open-circuit cathode potential also changed with a reduction in cathode area. At cathode areas of 0.25 to 1 square inch, the open-circuit cathodic potentials of growing pits did not vary appreciably with time. This, of course, did not apply to specimens showing creeping cathode potentials (Figure 4). However, after the open-circuit potentials of such specimens settled at a steady value, the above behavior was observed. The open-circuit cathodic potentials of the specimens with small cathode areas (0.020 square inch or less) varied rapidly with time. Immediately after open-circuiting, the potentials usually shifted rapidly to a more noble potential and then gradually became more anodic with time. The initial shift in the noble direction indicates that a localized depletion of ferric ions (concentration polarization) existed at the small cathode electrodes during pit growth. The potential shift was caused by the diffusion of ferrous ions away from the electrode surface.

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Figure 4—Effect of time on instantaneous polarization curves in 0.2$\overline{M}$ FeCl$_3$ + 0.05$\overline{N}$ HCl. Cathode area = 0.25 sq. in. Anode wire diameter = 20 mils.
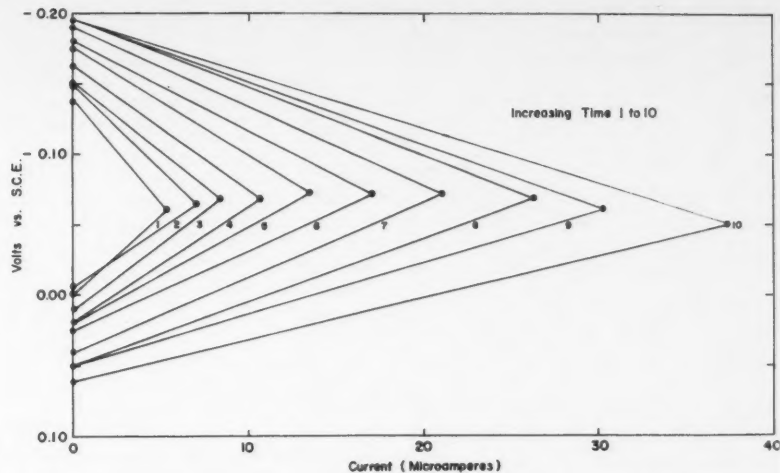
Figure 5—Effect of time on instantaneous polarization curves in 0.2$\overline{M}$ FeCl$_3$ + 0.05$\overline{N}$ HCl. Cathode area = 0.020 sq. in. Anode wire diameter = 20 mils.

Figure 6—Effect of time on instantaneous polarization curves in 0.2$\overline{M}$ FeCl$_3$ + 0.05$\overline{N}$ HCl. Cathode area = 0.013 sq. in. Anode wire diameter = 31 mils.

pit specimens appeared to decrease with decreasing cathode area. The specimen with the 0.003 square inch cathode electrode showed a very slow increase in pit activity with time. However, because of the non-reproducible nature of pit growth, quantitative correlations between cathode electrode size and growth characteristics could not be made.

A reduction in the cathode electrode area can be considered equivalent to three different circumstances that arise during pitting attack. First and most obvious, a reduction in cathode size is equivalent to the reduction of the area of a specimen in any ordinary corrosion test. Thus, the cathode electrode area studies can be used to show how the polarization characteristics of a single pit change with specimen area.

Secondly, the reduction of the cathode electrode area can be considered qualitatively equivalent to the enlargement of the pit anode. In either case, the ratio of cathode/anode area decreases. If the effects of cathode area reduction are applied to the enlargement of a single pit, the absolute electrode sizes in the two systems are not identical. The absolute size of a corroding system can have a pronounced effect on its polarization characteristics.[4, 5] However, the relatively high conductivity of the electrolyte and the almost uniform cathode current distribution, to be shown later, indicate that such comparisons are probably valid for the systems studied.

Third, the reduction of the cathode electrode area is equivalent to the existence of other pit sites on the cathode sheet. Such area reductions increase the cathodic current density at a given value of pit corrosion current as would the existence of other pits on the unpainted cathode electrode. An actively growing pit specimen with a cathode area of 0.01 square inch is equivalent to a pit specimen with a 1 square inch cathode electrode containing 99 random pit sites,

each with an activity equal to the pit under study.[1] When instantaneous polarization measurements are made on a reduced area pit specimen, the cathodic current density falls to zero. Hence, the polarization changes produced by cathode electrode reductions indicate how the electrochemical characteristics of all pits change as their number per unit area increases.

Electrochemical Control

The type of electrochemical control operating during pitting corrosion has been disputed.[2] From the preceding polarization diagrams, all types of control occur during pitting attack. Figure 3 illustrates a series of polarization diagrams showing complete anodic control. Polarization Diagram 2 in Figure 6 demonstrates a high degree of cathodic control, and Figure 5 shows a series of diagrams under mixed control.

(1) This assumes that the current is distributed evenly over the entire cathode electrode. This condition is approximated by the system studied. See section entitled Cathode Current Distribution.

From the results of the cathode area studies, it is evident that as pitting corrosion progresses, the electrochemical control shifts from anodic to cathodic control via mixed control. The progress of pitting corrosion refers to the enlargement of a single pit or the appearance of more pit sites on the exposed area. This observed shift in control type is identical to that predicted by Standifer.[6]

The concept of electrochemical control must be modified when applied to pitting corrosion. One must think in terms of an instantaneous electrochemical control. However, in view of the complex, time-dependent phenomena that occur during the progress of pitting attack, the type of control at any instant is of minor importance.

Effect of Anode-Cathode Separation

The artificial pit specimens used in this study differed from actual corrosion pits in that there was a finite separation between the anode and cathode electrodes. Although this separation was very small, it still represented a departure from the geometry of actual pits.

Figure 7—Effect of time on instantaneous polarization curves in 0.2M FeCl₃ + 0.05N HCl. Cathode area = 0.003 sq in. Anode wire diameter = 20 mils.
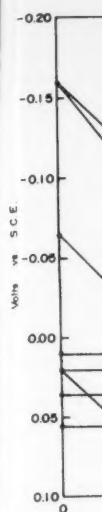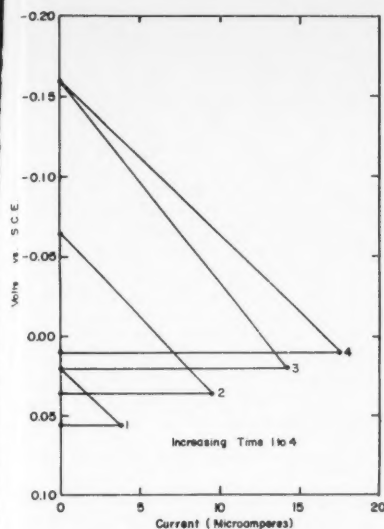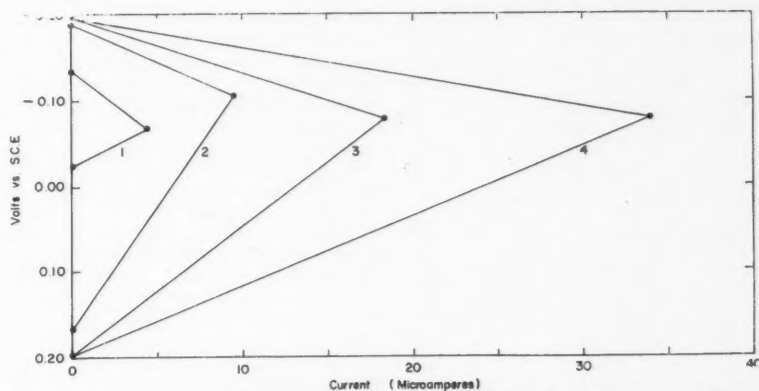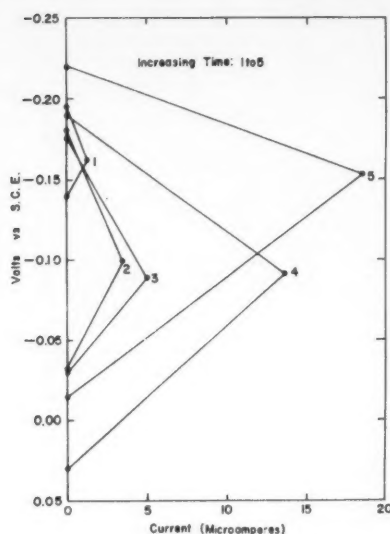

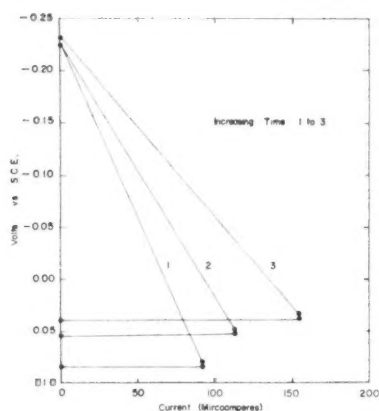Figure 8—Effect of anode-cathode separation on instantaneous polarization curves in 0.2M̄ FeCl₃+0.05N HCl. Cathode Area: 1.0 sq. in. Anode wire diameter = 20 mils. Separation = 0.120 in.
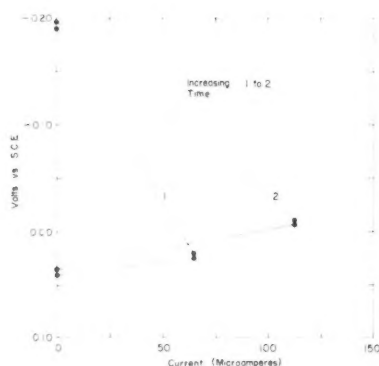

Figure 9—Effect of anode-cathode separation on instantaneous polarization curves in 0.2M FeCl₃+0.05N HCl. Cathode area 0.120 sq. in. Anode wire diameter = 20 mils. Separation = 0.120 in.
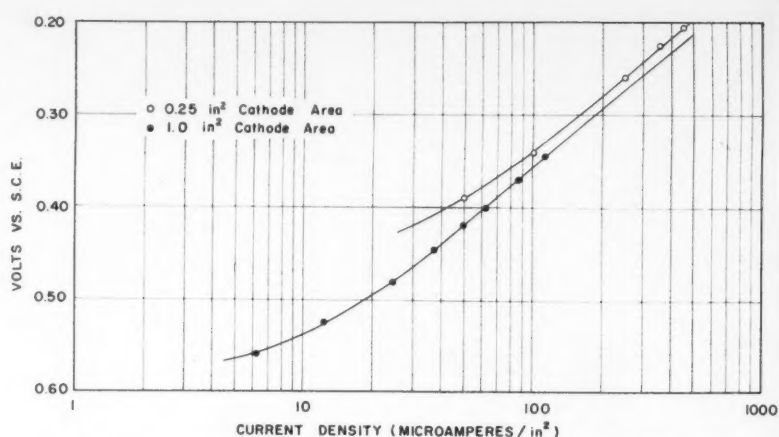
Figure 10—Impressed current cathodic polarization curves for pit specimens immersed in 0.1M̄ ferric sulfate.

The effect of this anode-cathode separation on pit behavior was checked by constructing several pit specimens with large separations.

Figures 8 and 9 illustrate the polarization diagrams obtained with the specimen having the greatest anode-cathode separation. This special specimen behaved similarly to the standard specimens. As evidenced by the high corrosion currents, the special specimen showed a rapid growth rate. Also, reduction of the cathode area produced effects similar to those observed with standard specimens. The only observable difference between this special specimen and standard specimens was the corrosion potential behavior. With standard specimens, the potentials of the anode and cathode electrodes under short-circuit conditions were always within approximately 2 millivolts of each other. However, the special specimen consistently showed a potential difference of approximately 3 to 5 millivolts under the same conditions. Ranges of the observed potential differences lay at the limit of accuracy of the pH meter. Hence, the actual magnitude of the difference between the two types of specimens is questionable. It was concluded that the anode-cathode separations of the standard pit specimens did not affect their similarities to actual corrosion pits.

Cathode Current Distribution

The fact that large anode-cathode separations did not affect markedly the polarization characteristics of the pit specimens indicated that the current distribution on the cathode electrode was nearly uniform. Additional tests were performed to determine cathode current distribution. Impressed current polarization studies were conducted using artificial pits immersed in 0.1 molar ferric sulfate. The specimens were allowed to remain open-circuited in the ferric sulfate until the cathode reached a steady potential value. The cathodic polarization curves were obtained by two different methods: by impressing current through the anode wire or through an auxiliary horizontal anode. If the cathodic current is evenly distributed over the entire cathode electrode, the polariza-

tion curves obtained by the above methods should be identical. Tests using specimens with cathode areas of 1.0 and 0.25 square inches indicated that either method produced almost identical polarization curves. Likewise, if the cathodic current is evenly distributed, then polarization curves obtained by impressing current across a pit specimen should be independent of cathode electrode areas.

The cathodic polarization curves obtained by impressing current through pit specimens with 1.0- and 0.25-square inch cathode electrodes are shown in Figure 10. The open-circuit potential of the 1 square inch specimen was 0.600 volt; that of the 0.25 square inch specimen was 0.499 volt. The difference is caused by the area/perimeter effect. Because of this, tests were not performed on smaller cathode electrodes. As Figure 10 illustrates, the curves are almost identical, indicating that cathodic current is almost uniform. Experimental errors probably caused the observed difference between the curves.

The uniform current distribution and the horizontal cathodic polarization curve of a 1 square inch cathode electrode explain why no pit interaction was observed with the double pit specimens used in a previous study.[1] The current generated by a single pit did not affect the potential of the cathode electrode (Figure 3) and, since the current distribution was almost uniform, the pit would not influence the activity of another pit adjacent to it.

Analysis of the Electrochemistry of Pitting

As shown by the results of the pit growth and polarization studies, pitting corrosion is an extremely complex phenomenon. The following analysis is a generalized and simplified explanation of the observed behavior of pitting attack. No attempt has been made to relate pitting corrosion to any specific theory of passivity. Indeed, this is one of the weaknesses of many of the theories and explanations of this mode of attack. Instead, the analysis is based on the observed behavior of passive surfaces. A

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generalized analysis of pitting consistent with the known properties of the passive state will have a more lasting value than one which has been rationalized to include a particular theory of passivity.

Mixed Potential Concept

The mixed potential concept states that, if an electrode is immersed in a solution containing an oxidation-reduction system, its open-circuit potential will depend on the electrochemical reactions which occur on its surface. If the electrode is chemically inert, its potential will be equal to the oxidation-reduction potential of the system. However, if the electrode is attacked by the solution, the open-circuit potential will lie between the oxidation-reduction potential of the system and that of the metal dissolution reaction. This potential is the mixed potential. Associated with this potential is a local action current on the electrode surface which is equivalent to the corrosion rate of the metal.

The mixed potential concept was first proposed by Wagner and Traud[7] and was discussed by Kolthoff and Miller,[8] Petrocelli,[9] and Stern and Geary.[10] Although the mixed potential theory does not depend on the concept of discrete anodic and cathodic elements, this concept can be treated as a special case under the theory. In this analysis, the idea of local elements is used for the sake of simplicity.

Local Action on Electrodes

The reversible oxidation-reduction potential of a ferric salt solution varies between approximately 0.65 and 0.75 volt (vs saturated calomel electrode), depending on the amount of ferrous ion present.[11] However, the cathode electrode potentials of the pit specimens were always observed to be more active than this in ferric chloride solutions. Therefore, the cathodic electrode potentials of a pit specimen are actually mixed potentials, and local corrosion currents exist on its surface. Likewise, the pit anode potentials are also mixed potentials; hence, cathodic reactions occur on its surface.

The electrochemical characteristics of pitting corrosion can be interpreted by three interdependent, instantaneous polarization curves as shown in Figure 11. E_a^o and E_c^o are the reversible electrode potentials for the anodic and cathodic reactions. I_a and I_c are the currents flowing between the local elements on the electrode surfaces. I_{corr} is the corrosion current flowing between the two electrodes. E_a and E_c are the instantaneous open-circuit electrode potentials. It is important to note that E_a and E_c would be equal under steady-state, open-circuit conditions.

Figure 11 is schematic, and linear polarization diagrams have been chosen for purposes of simplicity. The first diagram represents the superposition of all the local action currents occurring on the pit anode. The second diagram gives the current between the local elements on the cathode electrode surface. The last
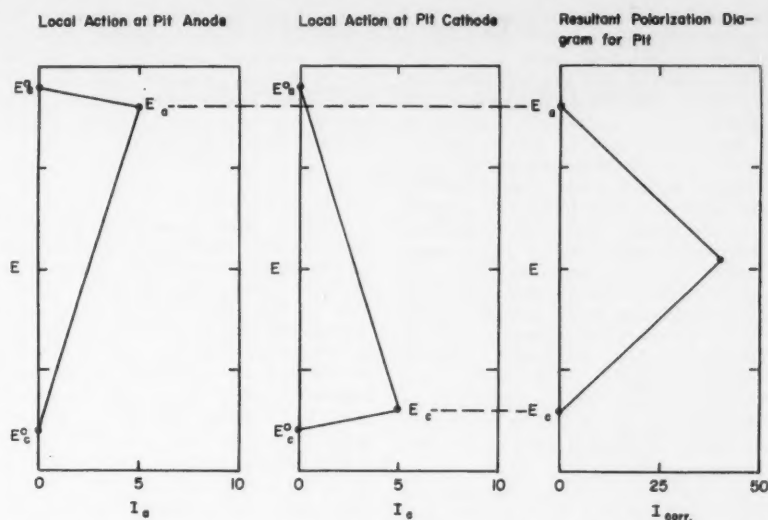
Figure 11—Relation between local action at pit anode and cathode and overall polarization behavior. I_a = local action at pit anode, I_c = local action at pit cathode, I_{corr} = resultant polarization diagram for pit.
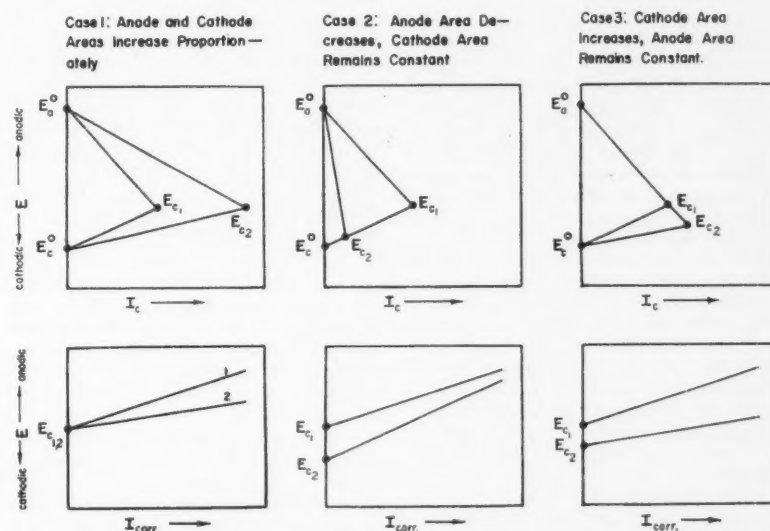
Figure 12—Effect of varying anode and cathode areas on the polarization characteristics of a corroding cathode.

diagram illustrates the resulting instantaneous polarization behavior of the two electrodes. The first two diagrams were arbitrarily drawn. The final, resultant polarization diagram was constructed from the two local action diagrams by a method described by Pope.[12] Thus, the open-circuit potential and the polarization behavior of a mixed potential electrode are related directly to the local cell reactions on its surface.

Figure 12 schematically illustrates how the electrochemical characteristics of a mixed potential or corroding cathode change as a result of changes in its local cell action. The upper diagrams are local cell polarization diagrams corresponding to the second polarization diagrams in Figure 11. The lower curves are the resultant cathodic polarization curves, corresponding to the cathodic polarization

curve in the final diagram of Figure 11. The anode area is the total area of the anodic elements on the surface. The cathodic area is the combined area of all the non-corroding cathodic elements. As the three cases illustrate, variations in local cell action have a pronounced effect on the electrochemical characteristics of a mixed potential cathode.

Effect of Time and Current

The effects of time and corrosion current flow on the electrochemical behavior of pitting attack are mutually dependent. The time-dependent changes are dependent on the existence of corrosion current flow. Therefore, only the observed changes in terms of both of these variables can be discussed. The observed changes in electrochemical behavior that occurred during the progress

of pitting attack are most unusual. The cathode electrode became more noble, and the anode became more active.

The causes of this unusual effect can be explained by referring to Figure 12. Cases 2 and 3 illustrate that a reduction in the relative area of the anodic elements on a corroding cathode shifts its potential in the noble direction. This must have occurred during the progress of pitting attack. Time and current flow suppressed anodic sites on the cathode electrode surface. The changes in the electrochemical behavior of the pit anode can be attributed to an increase in the relative anodic element area with time and current flow. As pitting corrosion progresses (Figure 11), the local action polarization curves are constantly changing. E_a and E_c move further apart with time while the values of E_a^o and E_c^o remain fixed.[2]

The reasons are not known why the local cell distribution changes with time and current flow. Changes in the electrochemical activity of metal surfaces with current flow and time have been observed by numerous investigators. Pearson[13] found that the minimum cathodic current necessary to protect buried iron structures decreased with time, indicating that the iron surface became more noble. Pryor[14] and Pryor and Keir[15] also have demonstrated the ennoblement of iron by cathodic currents. These investigators used instantaneous polarization techniques similar to those of the present investigation.[16] Recently, Okamoto, Nagayama and Sato,[17] using an ingenious rapid polarization device, observed that iron immersed in dilute sulfuric acid became more active after the application of anodic currents and more noble after the passage of cathodic currents. The magnitude of the changes produced was highly dependent on the intensity and duration of current flow.

The changes in the instantaneous polarization diagrams shown in Figures 3 to 7 are experimental evidence of the autocatalytic nature of pitting. Not only do these diagrams offer further proof for the conclusions of previous experiments,[1] but they also illustrate the mode of this autocatalytic nature. If the pit anode is considered, the changes induced by time and current flow tended to increase pit activity. Further examination of the polarization diagrams obtained with pit specimens having reduced cathode area

(2) Actually, E_a^o and E_c^o at the pit anode will vary because of the compositional changes within the pit cavity. For simplicity, these changes are not considered in this discussion.

leads to an interesting conclusion: the autocatalytic nature of pitting corrosion is not restricted to action at the pit anode. Pitting corrosion produces self-stimulating electrochemical changes at both anode and cathode areas. This is demonstrated in Figure 5.

Pit Anode Definition

Since the anode wire of the pit specimens did not corrode uniformly, the shift of the anodic open-circuit potential in the active direction is due to the enlargement of the corroding area with time. This introduces the question of defining the pit anode. If the pit anode is defined as that area on which only anodic reactions occur, then it would not be a mixed potential electrode. The open-circuit potential of this electrode would equal E_a^o in Figure 12 and there would be no local action currents. The only effect of time and current flow would be a decrease in the slope of the anodic polarization curves. The instantaneous open-circuit potential would remain constant. However, if the pit anode is defined so as to include some cathodic area, as is necessary in the present study, then an anodic potential shift would be observed with the passage of time and corrosion current. The latter definition is probably more realistic because there are undoubtedly some rapidly corroding areas within actual pit cavities that also support cathodic reduction reactions. With either definition, the observed electrochemical behavior during pitting corrosion would be nearly identical.

Summary

1. The electrochemical behavior observed during pitting corrosion has been analyzed on the basis of the mixed potential theory. A new concept of the electrochemistry of pitting corrosion has been proposed.

2. To completely describe pitting attack, an infinite series of rapid or instantaneous polarization diagrams are required since ordinary polarization curves are not applicable to this type of corrosion.

3. The concept of electrochemical control must be modified when applied to pitting corrosion.

4. The autocatalytic nature of pitting corrosion has been further clarified. Pitting corrosion produces self-stimulating electrochemical changes at both anode and cathode areas.

5. In ferric chloride solutions, the neg-

ligible interaction between two closely spaced isolated pits has been shown to be caused by the uniformity of cathodic current distribution and the weak polarization of the metal surface surrounding the pit sites.

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Any discussions of this article not published above will appear in the June, 1959 issue

Deterioration of Wood
By Marine Boring Organisms
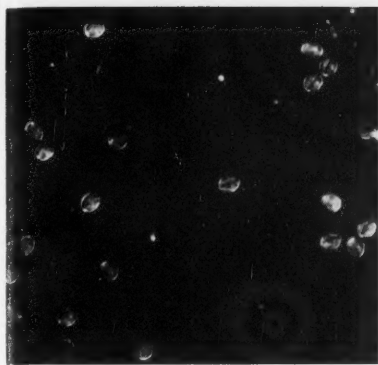
By H. HOCHMAN

Figure 1—*Teredo* larvae.
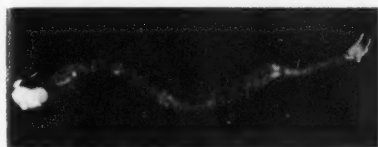
Figure 2—Adult *Teredo* containing larvae.
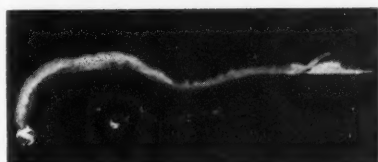
Figure 3—Adult *Teredo* and *Bankia*.
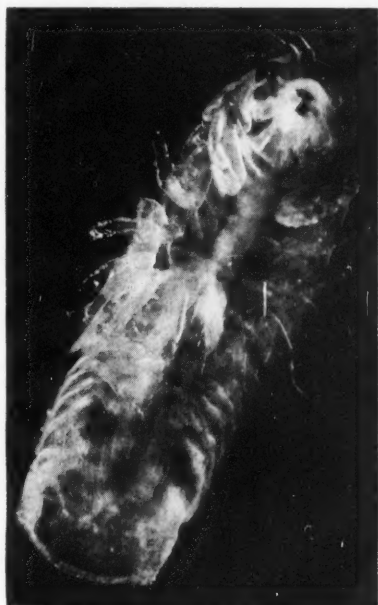
Figure 4—*Limnoria tripunctata*, ventral view.

Introduction

THE DESTRUCTION, by marine boring organisms, of wooden structures exposed to the sea has plagued man since the dawn of history. Although many devices have been employed to combat their destructive activities, marine boring organisms cause an estimated 50 million dollars worth of damage each year to water front structures along the coasts of the United States. In addition to these costs is the inconvenience that occurs when piers and ships are removed from service during their reconstruction period.

The rate at which untreated timbers can be destroyed by marine boring organisms can be illustrated by a situation that occurred in Hawaii and was reported by Dr. C. H. Edmondson of the Bernice P. Bishop Museum.[1]

In the process of laying an outfall sewer off Sand Island in Hawaii, a long trestle was constructed of untreated Douglas fir from which the heavy equipment required to handle the huge concrete pipe was to operate. Danger from marine borers was realized, but since the project was to be completed in eight months, the construction company considered the use of treated structural timbers any unnecessary expense. In 70 days, sections of the trestle collapsed, plunging considerable heavy equipment including diesel engines into the sea. The equipment was recovered, but valuable time was lost in removing what was left of the trestle and completing the job from floating barges.

Natural Resistance of Wood

All wood species tested for resistance to marine boring organisms have been damaged by these organisms. The rate of damage, however, varies considerably for different species and in different harbors.

Douglas fir is readily attacked by marine borers[2] as are most native American wood species used for marine piling. There are a few woods, however, that have gained reputations for resistance to marine borers. Among these are the South and Central American woods Greenheart and Angelique and the Australian turpentine wood.

Although resistant woods may withstand borer attack for long periods of time in some harbors, they are readily attacked in other harbors. For example, Greenheart piles rated as being in good condition after 80 years in the harbor of Liverpool, England, were attacked in

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Abstract

Most untreated woods are readily attacked by marine boring organisms. Some woods are naturally resistant to attack by some borer species and serve well in some harbors. Present standard wood preservative treatment, creosote or creosote-coal tar impregnation, is satisfactory in arctic and temperate waters but does not give long-term protection in tropical and sub-tropical waters. Although creosote prevents attack by the Teredine or shipworm type of marine borer and by two of the three species of *Limnoria* present in U. S. harbors, one species, *Limnoria tripunctata*, which thrives in warm waters, successfully attacks creosoted wood. Because many Navy waterfront structures are located in areas where early failure of creosoted wood occurs, the Bureau of Yards and Docks is investigating the marine borer problem.   3.3.3

four years at Salem, England, and failed in Java, India, in five to ten years.[3, 4]

In addition to the variable resistance to marine borers offered by resistant woods in various harbors, the same species of wood grown on different soils may differ considerably in both composition and resistance. Turpentine wood, *Syncarpia laurifolia*, is used extensively as a pile timber in Australia. In exposure tests in Honolulu harbor, Australian grown turpentine wood was lightly attacked by *Teredo* and showed moderate superficial action by *Limnoria* after four years.[5] Blocks of the same species grown in Hawaii were often badly damaged in five months. Chemical analysis showed the Australian grown wood to contain up to 1.25 percent silica; the maximum silica content of Hawaiian grown wood was

0.17 percent. The averages of a number of samples were 0.59 percent and 0.091 percent, respectively.

Some correlation seems to exist between the silica content of wood and its resistance to marine borers. Woods with a high silica content, with few exceptions, are more resistant than woods of low silica content.[6] To determine the effects of increasing the silica content of wood, southern yellow pine blocks were impregnated with silica. The borer resistance was increased. Untreated blocks were destroyed in three to six months while panels impregnated to a high silica content were only lightly damaged after two years. Unfortunately, although the resistance to wood borers had increased, the resultant product appeared to be suitable for rock boring pholads. A number of panels were severely damaged by these animals.

Some resistant woods do not have a high silica content. Examples of such woods are Greenheart and *Lignum vitae.* The resistance of some of these woods has been attributed to their alkaloid content[7] and the author's laboratory is now engaged in isolating and identifying the alkaloids of Greenheart.

It should be noted, however, that in no case have woods of high silica content been low in borer resistance although a few woods of low silica content may be resistant because of their alkaloid content or for other reasons.

It can be seen from the preceding discussion that naturally resistant woods can be used for waterfront structures in some harbors, but the number of harbors in which they can be used without preliminary investigation is comparatively small.

The term marine borer has been generally used to include those marine invertebrates which drill into and consequently damage timber and other solid objects in salt water. Other destructive marine borers may cause considerable economic loss to industry, such as the boring sponge which perforates the shells of oysters. In this paper, the definition will be restricted to those marine invertebrates which attack wooden structures.

Marine Borer Groups

The animal organisms responsible for the biological deterioration of wooden marine structures are members of two main groups. The first group is composed of animals from the phylum *Mollusca.* In their larval stages, they are oyster or clam-like in appearance and metamorphose into worm-like animals as they bore into wood. Members of this phylum are responsible for the rapid destruction of timbers exposed in a marine environment. The particular genera involved are the *Teredo* and *Bankia* of the family *Teredinidae* and the pholad *Martesia.*

The second group of organisms is comprised mainly of species of the genus *Limnoria* and in some harbors by members of the genus *Sphaeroma.* They are shrimp-like in appearance, about ⅛-inch to ¼-inch long, and generally burrow just beneath the surface of the wood. These animals have been described as having the body of a shrimp and the head

of a termite. They are responsible for the wood destruction readily visible on surface inspection of wood.

Life Cycles

The molluscan or teredine borers begin their existence as free-swimming larvae, shown in Figure 1. The two *Teredo* species, *Teredo navalis* and *Teredo diegensis,* found on the West Coast of the United States, are bisexual. Fertilization and development of the larvae occurs within the body of the animal, and the mature larvae are ejected into the sea through the excurrent siphon of the animal. At this stage the larvae of *Teredo diegensis,* the only species identified at Port Hueneme, are about 250 microns (0.01 inches) in diameter. They must attack wood within 48 hours or they lose their ability to bore successfully into wood. They crawl on the surface of the wood by means of an amoeboid projection called the foot until they find a place suitable for boring. Once an animal has bored into wood, its life cycle is completed in that piece of wood.

Four significant changes now take place: (1) A serrated projection develops at a 90-degree angle to the original shell hemispheres; (2) Siphons develop which permit the animal to pump sea water through its body; (3) The clear chitin shell of the larva starts to calcify; and (4) The animal begins to elongate (Figure 2) with the shell or boring end proceeding into the wood and the siphon end remaining at the original site of penetration.

The only *Bankia* species of any significance on the west coast of the United States is *Bankia setacea,* shown in Figure 3. Like all other members of this genus, and in contrast to some species of *Teredo,* adult animals eject sperm and eggs into the sea where fertilization takes place. Swimming immature larvae are developed within a few hours. The larvae develop for about a month before they are ready to attack wood. After wood is attacked, the *Bankia* larvae metamorphose in a manner similar to that of the *Teredo.*

No *Martesia* are found in harbors of western United States, but these borers are found in Hawaii and other Pacific islands. These animals differ from the Teredine borers in only one major respect: the metamorphosis into a worm-like structure does not take place. As a result, the animals burrow just below the surface, enlarging the burrows as they grow.

The crustacean borers resemble a sow bug in appearance, Figure 4. The most common wood borers of this class are members of the genus *Limnoria,* also known as the gribble. The body of the animal is from ⅛-inch to ¼-inch in length and is about one-third as wide. Their seven pairs of legs have sharp, hooked claws which enable the animals to cling to wood and move freely on its surface. They burrow just below the surface of the wood and form a series of tunnels. Menzies[4] found that at a low population density there are only two animals in each tunnel, one male and one female, with the female in the blind end of the tunnel.

The female carries the eggs in a brood pouch on the underside of the body between two rows of legs. The number of eggs in a single brood is seldom less than six or more than seventeen. When hatched, the young differ only in size from the adult and are ready to bore at once. They begin to bore near the parent so that *Limnoria* infestation generally spreads from a center. Heavily infested wood may contain 300 to 400 animals of all ages per square inch.

Three *Limnoria* species are found along the western coast of North America.[8, 9, 10] They are shown in Figure 5. The species *Limnoria lignorum* is found from Alaskan waters as far south as Point Arena, California. Between Point Arena and Port Hueneme or Los Angeles, California, the predominant *Limnoria* species is *Limnoria quadripunctata,* and *Limnoria tripunctata* is the principal species in Los Angeles harbor and southward. The relationship between *Limnoria* species and water temperatures has been pointed out by Menzies. The *Limnoria lignorum* requires cold waters, *Limnoria tripunctata* requires warm waters with *Limnoria quadripunctata* requiring an intermediate temperature.

The largest crustacean known to damage wood is the *Sphaeroma.* While their burrows are much larger than those of *Limnoria,* the animals themselves are not as numerous nor as destructive. They are reported to exist along the Pacific Coast as far north as Alaska and have been found in test boards outside San Francisco Bay. They appear to prefer very soft wood and do not constitute a serious economic problem.

Examination of Damage

Examination of a cleaned block of ¼-inch laminated southern yellow pine that had been exposed in Hueneme harbor for eight months, Figure 6, shows little structural damage caused by marine boring organisms. Figure 7 is a magnified view of *Limnoria* in their burrows just below the surface of untreated wood.

Close examination of the block while it is still in the sea water, Figure 8, shows the siphons of the teredine borers projecting from the surface. This is the only evidence of the presence of the shipworm type of borer that is visible on surface inspection of the block. Even these, however, may not be seen unless the block has just been cleaned to remove fouling organisms.

Sawing the block into two parts, Figure 9, or separating the lamina, Figure 10, shows the severe structural damage which the shipworms have caused. The larger holes are caused by *Bankia setacea* which, in Hueneme harbor, can grow to a length of 10 to 12 inches in eight months. The smaller holes are caused by *Teredo* present in Hueneme harbor, where they seldom grow to lengths of more than 5 or 6 inches.

Methods of Treatment

Since man first recognized the shipworm problem, many remedies have been tried. The earliest means of combatting borers probably consisted of anchoring

Figure 5—

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Figure 5—*Limnoria* species: *lignorum, tripunctata* and *quadripunctata.*

Figure 6—Exterior of laminated test block.
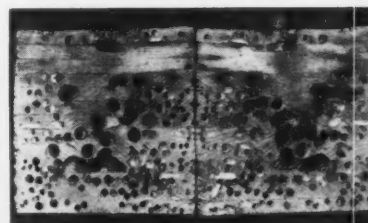
ships upstream from river estuaries. In addition to killing any shipworms that were in the wooden hulls, this procedure also caused fouling organisms to drop off of the sides and bottoms of the vessels. As ships traveled further and further from shore and were away from their harbors for longer periods of time, other procedures were inaugurated. These included such practices as applying brews and concoctions of many kinds, metal sheathing and scupper nailing. Some of these methods have persisted for many years. Fishermen in Iran, for example, still bring their fishing vessels out of the water periodically and apply a concoction prepared from local berries to the entire hull.

The most satisfactory method which has been developed for the preservation of wood in a marine environment is the practice of creosoting. In some harbors, especially the cold water harbors, creosoted timbers have lasted 30 years and more. In warmer harbors, however, creosoted pilings, just like some of the naturally resistant wods, do not last longer than 10 to 15 years. More recently the practice of incorporating coal tar into creosote has given protection for longer periods of time.

The incidence of early failure of creosoted timbers coincides to a considerable extent with the presence of *Limnoria tripunctata.* These animals apparently can live in the presence of high concentrations of creosote, as seen in Figure 11. As they erode away the creosoted surface, the lightly treated or untreated portions of the structure are exposed. The structure can be attacked now by the shipworm type of organism and is destroyed in a relatively short period of time. Any new treatment should, therefore, be aimed primarily at the *Limnoria* species of borer.

Admiral E. V. Dockweiler and Carrol M. Wakeman of the Los Angeles Harbor Department have allowed the author to present the following account of a pier in a *Limnoria* infested area of Los Angeles Harbor:

"In the year 1913, or the early part of 1914, a number of Douglas fir piles were driven in the wharf system at Berths 57-60, Los Angeles Harbor. They were given a nominal 16-pound treatment with Grade I creosote. These piles were removed in 1924 because of a change in the design of the wharf facility, but it was noted that deterioration caused by *Limnoria* attack was in advanced stages. A new apron wharf was constructed at the same location in the same year (using 16-pound creosoted Douglas fir piles). In
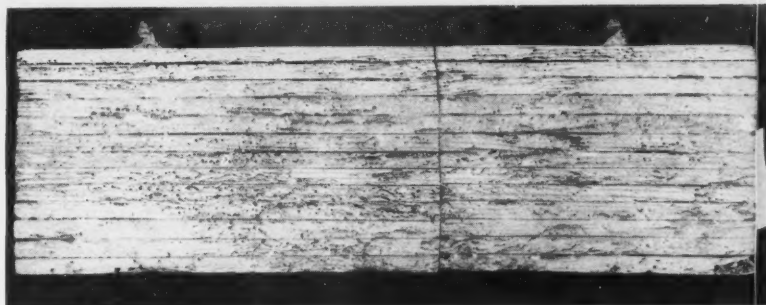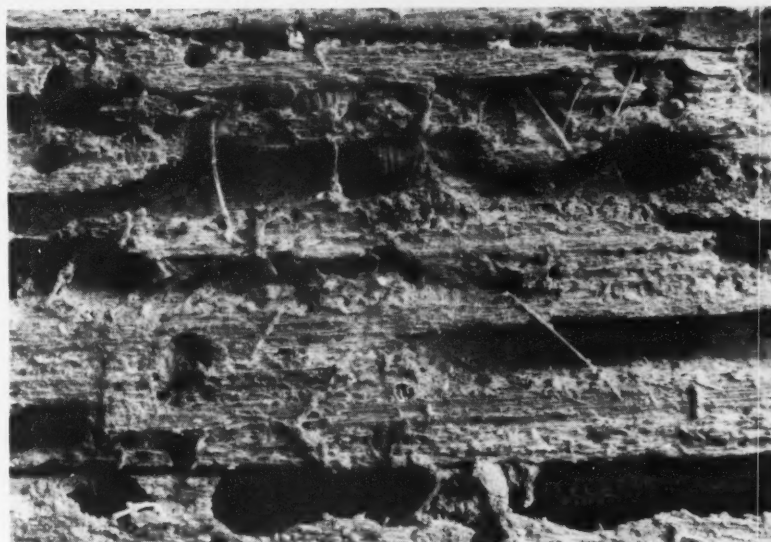

Figure 7—*Limnoria* burrows in untreated pine.

Figure 8—Siphons of Teredine borers.

Figure 9—Interior of laminated test block.

Figure 10—Separation of laminations of test block.

1939, after 15 years service, this wharf suffered a complete collapse, again because of the ravages of *Limnoria*."

When the pier collapsed, shown in Figure 12, a railroad car of scrap steel was deposited at the bottom of the harbor.

Because creosoting does not produce

piling of sufficient durability in many harbors, numerous other treatments have been evaluated as marine borer deterrents. Among these are a number of
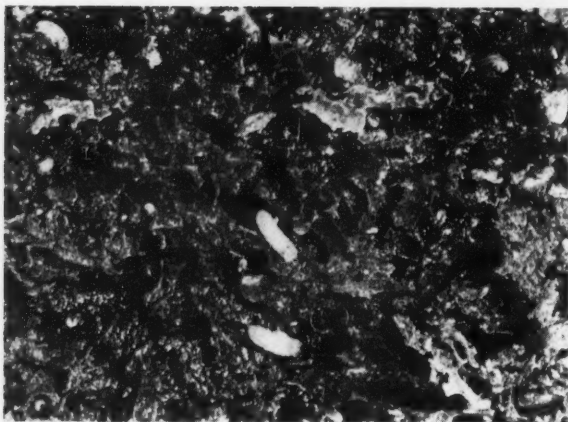
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Figure 11—*Limnoria* burrows on creosoted pile.

Figure 12—Wharf destroyed by borers after 15 years in Los Angeles Harbor.

copper-containing compounds such as copper naphthenate, copper pentachlorophenate, copper fluoride and copper arsenate. In all instances, where sufficient exposure data are available, these treatments fail after a few years. Impregnation with several plastics has shown some promise. Woods, however, differ widely in their ability to take such treatment. No treatment other than the incorporation of coal tar in creosote has demonstrated a superiority to creosote. In some instances more testing must be done before complete evaluations can be made.

Current Research

Because of the extensive waterfront structures required by the Navy, the Bureau of Yards and Docks has instituted a systematic investigation of the whole marine borer problem. One part of its program is to fractionate creosote and determine the borer resistance of the various fractions. This study is being conducted jointly by the Naval Research Laboratory, Washington, D. C., and the Marine Biology Laboratory of the University of Miami, Miami, Florida. The William F. Clapp Laboratories, Duxbury, Massachusetts, are investigating the distribution of the various species of borers in many harbors throughout the world.

The U. S. Naval Civil Engineering Laboratory of the Bureau of Yards and Docks is engaged in several phases of this program.

First, the alkaloids of greenheart are being investigated. These compounds are toxic to marine borers. The structures of these compounds will be used as a basis for the synthesis of impregnating materials that can be applied to more common woods.

Second, two toxicity screening procedures have been developed using adult *Limnoria tripunctata* and *Teredo diegensis* larvae as the test animals. Although both *Limnoria tripunctata* and *Limnoria*

quadripunctata are present in Hueneme harbor, the essentially pure culture of *Limnoria tripunctata* used in the screening tests is obtained from creosoted piles that have been in the harbor for several years.

Third, the effects on these animals of environmental conditions, such as temperature and salinity, are being studied. Attempts are being made to correlate the results of the toxicity tests with physiological functions as another means of developing more potent toxic agents.

Fourth, the factors involved in the retention of chemicals by wood are being studied because an extremely toxic agent is of little value if rapidly leached out of the wood.

Finally, those compounds which merit further study on the basis of the several screening procedures are impregnated into small wooden panels and exposed in Hueneme Harbor and in Pearl Harbor. There have been a number of systems that merited such evaluation. The tests on these materials have not progressed sufficiently to permit an evaluation of these systems at this time.

Ideal Wood Preservation

The properties of an ideal wood preservative for marine use may be summarized as follows:

1. The preservative must be toxic to boring organisms in very small concentrations. When a *Teredo* larva has grown to an animal only one centimeter long, a 3000-fold increase in volume has taken place. Thus, once a teredine borer gets a foothold in a piece of wood and begins to grow, the amount of toxic material required to stop it goes up almost exponentially.

2. The treatment must be resistant to leaching by sea water and must remain in the wood in toxic concentrations for many years.

3. The treating materials must be stable in a marine environment and must not be altered to a less toxic material. Thus, mercuric chloride is very toxic to borers, but the hydrogen sulfide present in almost all harbors would detoxify this substance by converting it to the non-toxic mercuric sulfide.

4. The preservative must penetrate the wood readily and not be filtered by the wood surface.

5. The preservative must not decrease the structural strength of the wood.

6. The preservative must not be corrosive to metal fastenings.

7. The preservative must be inexpensive.

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Any discussions of this article not published above will appear in the June, 1959 issue

If you could get a corrosion literature search at nominal cost...

Would you be interested in getting copies of abstracts of articles written about your corrosion problems if they were available at a nominal cost? During the past seven years NACE has accumulated a file of more than 16,000 abstracts which have been classified by subjects. The abstracts refer to literature published in about 1000 periodicals everywhere in the world and in hundreds of books.

This file is probably the largest collection of corrosion control information of its kind in the world available for unrestricted use. The wealth of information available is of almost incalculable value, and NACE wants to be sure it is being put to best use for the advantage of industry combating corrosion.

One service NACE may render is to make these 16,0[00] abstracts (and their cross-references) available in a sear[ch] service for those who only occasionally need to inves[ti]gate literature about their corrosion problems.

NACE needs to know how many are likely to use [the] search service and how often they are likely to use [it]. Charges will have to be of two kinds: A flat fee f[or] handling, probably less than $30. And, a charge [of] probably less than 50¢ per abstract located. in so[me] cases no abstracts will be in the file and the servi[ce] charge will net negative information only. In othe[r] numerous abstracts will be located.

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Report on Pipe Coating Leakage Conductance Discussed at New Orleans Committee Meeting

A discussion on the committee report published in the December, 1957, issue of Corrosion was held at the New Orleans meeting of Unit Committee T-2D on standardization of procedures for measuring pipe coating leakage conductance.

Those reporting recent experience in making field coating conductance measurements believed that good agreement can be expected in values obtained on the same section of line. The better the coating, the better the agreement in values obtained.

Inconsistencies experienced in determining the resistance of the calibrated sections of pipe for line current measurements were discussed. Tests made several years ago by one company showed no agreement in measured values of pipe resistance for the same section of a large diameter line using several values of calibration current. No end losses were detected, and the current leads were properly separated from the potential leads. No difficulty was experienced in using the same procedures on smaller diameter lines in the same area, according to the company representative.

No explanation was brought out during the discussion although it was pointed out that calibration currents used to determine the pipe resistance should be of the same magnitude as the currents to be measured.

Chairman L. F. Heverly stated that future activities of the committee need to be determined and that special cases mentioned in earlier reports need to be investigated. Work should be done on techniques involved in making certain measurements such as pipe-to-soil potentials, he suggested.

Committee Hears Reports On Coatings and Linings

Technical Unit Committee T-6A, Organic Coatings and Linings for Resistance to Chemical Corrosion, heard several reports at its October meeting in New Orleans.

A report by the Task Group on phenolics was reviewed by Chairman C. G. Munger, and progress on the Hypalon report was presented.

Report by the polyethylene task group was affirmatively voted on to be submitted to the Publications Committee for publication in Corrosion.

Vertis Volkening reviewed Dow Chemical Company's methods of screening coatings and linings in their laboratory and under actual field conditions.

A review of reports to be made at the Chicago meeting in March was also given.

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Over 70 technical committees will meet during the 15th Annual NACE Conference in Chicago.

A tentative schedule of the Technical Committee meetings at the Chicago Conference is printed on page 80.

Committee to Prepare Report on Coatings

Preparation of a report on recommended practices for the use of coatings in the oil field and gasoline plants was undertaken by Unit Committee T-6E at its October meeting in New Orleans.

The need was discussed for more information and recommendations on coatings directed toward the production superintendent, farm boss and petroleum engineer who may suddenly find themselves having to select, specify and inspect coatings.

The committee proposed that this information be gathered and published as a report and be considered as one of the committee's primary objectives.

Chemical terminology should be left out of the report, according to a consensus of the group. Only the physical properties of various types of coatings would be included. The report would include a table of recommended systems for various types of equipment and environments as compiled from a 1956 questionnaire Standard specifications will be included also.

Need for educational programs in the field was discussed. The Coatings School sponsored by the Houston Coatings Society was reviewed, and the Magnolia Paint School to assist field personnel in obtaining better coatings was described.

Plans were made to discuss the coatings report in detail at the Chicago meeting in March.

New Task Group Formed For Los Angeles Area

A new task group to deal with refinery corrosion problems in the Los Angeles area has organized and elected officers. It is designated as Task Group T-8B, Refinery Industry Corrosion, Los Angeles Area.

Officers elected recently are Chairman George C. Hall, Richfield Oil Corp, Wilmington, Cal., Vice Chairman W. G. Welter, General Petroleum Corp., Los Angeles, and Secretary E. B. Marquand, Aluminum Company of America, Los Angeles.

Meetings are held every other month with new members and guests welcomed to all task group activities. Meetings were held in October and December.

Task Group T-4F-1 Holds Roundtable Discussion

A round table discussion was held for the Boston meeting in October of Technical Task Group T-4F-1, Materials selection in the Water Industry.

Background of the Greater Boston Electrolysis Committee was presented to show that the committee was begun four years ago when extensive piping systems were introduced which crossed existing utility pipes and conduit. Serious problems resulted in the criss-crossing of gas pipes, water suuply lines, power lines and railroad tracks.

A short discussion was devoted to electrolysis problems within private homes in regard to the grounding of electric power and telephone lines to water pipe.

Work of the AWWA Valve Committee was presented to the group with the suggestion that T-4F-1 work with the Valve Committee to write valve specifications to benefit the industry as a whole. Because water corrosion problems vary throughout the country, one general specification would have to cover most applications with addenda for special situations, it was suggested.

Piping and valving problems experienced by one company were presented in the discussion. The committee was told that many of these problems were solved by the use of plastic materials, copper-nickel alloys and bronze on the equipment used to reduce the salt content of brackish and sea water for industrial and potable water supplies.

Task Group Future Plans To Be Discussed in May

Status and future plans for Task Group T-5G-1, Cooling Water Corrosion, will be discussed at a meeting set for next May in Houston. Suggested items for this meeting are pretreatment of metal, organic chelating inhibitors and slip stream filters. These plans were discussed at the group's October meeting in New Orleans.

Status of this group was discussed because it has completed all its primary objectives. Opinions of those present indicated that other objectives and problems will be arising which the group should consider. These objectives will be discussed at the Houston meeting in May.

New Committee Planned For Aluminum Pipe Work

Formation of a unit committee under T-2 Pipe Line Corrosion has been suggested to explore the possibility of cathodic protection of buried aluminum pipe lines.

An organizational committee meeting will be held in Chicago during the March conference.

NACE NEWS

Canadian Eastern Division to Meet Jan. 12-14

Paper, Marine and Chemical Industry Problems Considered

Program for the Eastern Divisional Meeting of the Canadian Region to be held January 12-14 has been announced. All activities and technical sessions will be at the Sheraton-Mount Royal Hotel, Montreal, Quebec.

Exhibits on the ninth floor will be open January 12 and 13 from 10 am to 10 pm and January 14 from 10 am to 2 pm. A schedule of technical papers to be presented is given below.

Monday, Jan. 12, Morning
Corrosion Research in the Pulp and Paper Industry, by R. B. Kesler, Institute of Paper Chemistry.
Corrosion Problems in Cooling Water Systems in Eastern Canada, by J. B. Hambley, Alchem Limited.
Some Practical Considerations of High Temperature Corrosion, by H. G. Bennett, British American Oil Co.

Monday, Jan. 12, Afternoon
The Use of Nickel in Corrosion Resistant Materials in the Mining, Milling, Smelting and Refining of Metals, by G. S. Farnham, International Nickel Co., Canada Ltd.
Practical Corrosion Problems in the Chlorine Industry, by M. Zundel, Vickers Krebs Limited.
The Materials Engineer in the Chemical Industry, by W. H. Burton, Allied Chemical Corporation.

Tuesday, Jan. 13, Morning
Polarization Curve Theory and Experimental Methods Developed for the Study of Corrosion and of Cathodic and Anodic Protection, by W. A. Mueller, Pulp & Paper Research Institute of Canada.
Oil Soluble Corrosion Inhibitors, by W. S. Quimby, The Texas Co.
The Use of Resin Elastomers and Bricks in Acid Resistant Linings, by B. Mohr, Chemical Engineer, Philadelphia.

Tuesday, Jan. 13, Afternoon
Some Notes on Cathodic Protection in Tidal Estuaries, by D. B. Bird, Aluminum Company of Canada, Ltd.
The Correct Alloys for Use as Condenser Tubes, by T. H. Rogers, Halifax Naval Research Establishment.
Probability and the Stress Corrosion Cracking of Copper Alloys, by D. H. Thompson, American Brass Co.

Wednesday, Jan. 14, Morning
Corrosion in Alkaline Pulping Digesters, by E. W. Hopper, Consulting Engineer, Pittsburgh.
Methods of Controlling Corrosion at Polymer, by N. Monsour, Polymer Corp., Ltd.
Paper by R. F. U. Icely, Carbide Chemicals Co.

Wednesday, Jan. 14, Afternoon
Corrosion Control in Petroleum Refineries Processing Western Canadian Crude Oils, by C. L. Easton, Imperial Oil Limited.
Corrosion of Copper and Copper Alloys, by D. S. Neill, Bridgeport Brass Co.
Paper by R. B. McIntosh, Sherritt-Gordon Mines Limited.

Conference Committee Chairmen
General chairman of the conference is H. G. Burbidge, Aluminum Company of Canada, Ltd.

Other committee chairmen are G. F. Drumm, registration, D. Evans, exhibits, H. A. Hencher, treasurer, E. T. Hurley, hotel, G. A. Lowles, technical papers and N. D. Woollings, publicity and advertising.

Wachter to Be Given 1958 Speller Award

Aaron Wachter, director of research, Shell Development Corporation, Emeryville, Cal., has been named to receive the 1958 Frank Newman Speller Award of the National Association of Corrosion Engineers. The award is made in recognition of Dr. Wachter's achievements in corrosion engineering.

The Whitney Willis Rodney Award will not be made for 1958, the committee having decided that there was insufficient information concerning the candidates to permit making a selection. This is the first time since the awards were initiated in 1947 that the committee has failed to recommend persons for both awards.

Wachter

The Speller Award, named after its original recipient, is made in recognition of achievements in the field of corrosion engineering.

Dr. Wachter, who was president of NACE in 1954, has long been active in the association in administrative and technical capacities. Besides serving as president, he was a member of the NACE board of directors, of technical committees and helped form the San Francisco Bay Area Section and was its first chairman. He has been author and co-author of technical papers on corrosion control published by NACE and elsewhere.

After receiving a BS in chemistry from City College of New York, he received a PhD in physical chemistry from University of California in 1930. He was National Research Fellow at California Institute of Technology in 1930-31 and at Johns-Hopkins University in 1931-32. He joined Shell Development in 1932 and in 1938 was named head of its corrosion department.

Short Course to Be Given in Kansas City

The Corrosion Control Short Course to begin this month at the College of St. Teresa in Kansas City, Missouri, has been outlined and the instructor named.

Offered in cooperation with the Kansas City Section, the course will be conducted in eight weekly sessions, each with one-hour lectures and one-hour question and discussion periods. Dates are to be announced later.

Course Outline
Eight areas are to be covered in the course:
1. The nature and mechanism of corrosion.
2. The influence of the metal on the corrosion process.
3. Principles and methods of corrosion testing.
4. Atmospheric corrosion and its prevention.
5. Underground corrosion and its mitigation.
6. Protective coatings (organic).
7. Study of current corrosion (electrolysis).
8. Cathodic protection.

Instructor Named
Albert L. Kimmel of the Midwest Research Institute will be instructor for the short course. Additional information on the course can be obtained by writing Mr. Kimmel at the Institute, 425 Volker Blvd., Kansas City 10, Missouri.

Section Meeting
A discussion on the economics of corrosion control was held at the November meeting of the Kansas City Section by J. C. Spaulding, Jr., Sun Oil Co., Dallas. Application of Nuclear Energy to Corrosion Problems was the December meeting topic by F. S. Rowland, University of Kansas.

Houston Short Course Program Is Complete

Final arrangements in the Houston Short Course program scheduled for January 22-23 have been made. The course will be held at the University of Houston.

The following information supplements that given on the tentative program on Page 95 of the December issue of CORROSION.

Lyle Sheppard, Shell Pipeline Corp., and C. C. Nathan, Texas Company, will be the speakers for the two parts of the session on internal corrosion.

Gordon Doremus, Cathodic Protection Service, will discuss instruments for corrosion measurement. Speaker for the session on rectifier installation and operation will be Troy R. Stilley, Good-All Electric Mfg. Co.

A. L. STEGNER
Treasurer

H. P. GODARD
President

GEORGE E. BEST
Vice-President

New Officers and Directors To Be Installed at Chicago

H. P. Godard, head of the chemical division, Aluminium Laboratories, Ltd., Kingston, Ont., has been elected president of the National Association of Corrosion Engineers. George E. Best, Solvay Process Division, Allied Chemical Corp., Baltimore, has been named vice-president. A. L. Stegner, Tennessee Gas Transmission Co., Houston, has been reelected treasurer for the third consecutive time.

Officers and directors take office on the last day of the NACE 15th Annual Conference in Chicago, March 16-20.

Barrett

Simons

Dr. Godard, in addition to being vice-president of NACE 1958-59, has been active in NACE affairs nationally, in Canadian Region and in connection with the work of technical committees. He has been a director, a member of the abstract subcommittee and chairman of the Inter Society Corrosion Committee. He has been a member of the Canadian Associate Committee on Corrosion Research and Prevention since its formation in 1947. Most of his corrosion work has been in connection with the reactions of aluminum.

Williams

George E. Best, technical adviser to the general manager of technical service, Solvay Process Division, was manager of technical service for Mutual Chemical Company before it was merged with Solvay. His long record of activity in NACE includes membership on the board of directors, membership in the executive committee, chairmanship of Baltimore Section, chairmanship of Northeast Region, member of technical program committees, awards committee, and symposia chairman. He has authored and published two papers on corrosion. He has been doing corrosion control work for 15 years.

Directors elected representing active members are J. P. Barrett, Pan American Petroleum Corp., Tulsa, and E. L. Simons, General Electric Research Laboratories, Schenectady. G. F. Williams, Dowell, a division of The Dow Chemical Co., Tulsa, Okla., was elected director representing corporate members. All will serve 3-year terms.

Jack P. Barrett, Pan American Petroleum Corp., Tulsa, well known among NACE members for his work with technical committees concerned with corrosion of petroleum equipment, was chairman of South Central Region and has held other regional offices. He has an AB in chemistry from William Jewell College and has been an NACE member since 1947.

Edward L. Simons, analytical chemist, General Electric Research Laboratory, has held numerous offices in NACE, including chairmanship of Northeast Region and of Schenectady-Albany-Troy Section. He received the NACE Young Author Award in 1956 for his co-authorship of a paper on sodium sulfate in gas turbines. He has been active in NACE technical committees in his field. He has a PhD in physical chemistry from New York University.

Guy F. Williams, who has been corporate representative for his company, Dowell, since 1949, is concerned with his company's activity in conection with oil and gas well special services and industrial chemical services as well as magnesium anodes. He has had many technical papers on corrosion published and is active in other organizations, including American Petroleum Institute, AIME and the Nomads.

133 Technical Articles and 24 Topics Published in '58

Publication of technical information in CORROSION during 1958 was at a level slightly under that of 1957, considering quantitative factors only. During the year 133 technical articles appeared in the technical section and 24 in the Technical Topics section. In the 1958 alphabetical index to authors 237 names are listed, compared to 244 in 1957; only 77 discussions are indexed, compared to 140 in 1957.

The alphabetical subject index occupies 6 pages, a 50 percent increase over the space occupied in the 1957 volume. The ratio of increase of the subjects indexed is about the same as the increase in space occupied. Subjects indexed also were greater than those in 1957 by about the same percentage.

Because of the change in type size, the number of pages occupied by the technical section in 1958 was a little over 40 percent less than the pages occupied in 1957.

Technical Section

Item	1957	1958	Diff.
Articles	135	133	—2
Authors	244	237	—7
Discussion	140	77	—63
Pages	842	598*	—244

*Smaller type reduced pages by about 40 percent.

Technical Topics Section

Articles	21*	24	+4

*July-Dec. only.

Northeast Region News

Genesee Valley Plans Water Softener Forum

A forum on water softeners is scheduled for the January 27 Genesee Valley Section meeting. Tentative panel includes Gil Cox of International Nickel, Al Levy and Dave Priest of the Pfaudler Co., Nelson Carter of Eastman Kodak, Ross Tucker of Niagara Mohawk and R. N. Stenerson of Carrier Corp.

Results of salt test corrosion panels placed on automobiles will de discussed at the February 25 meeting.

Discussion of corrosion problems and possible solutions as suggested by the members was held at the November meeting.

New York Jan. 14 Meeting To Discuss Epoxy Coatings

H. W. Howard of Shell Chemical Corporation will speak on Use of Epoxy Coatings in Resistant Coatings at the January 14 meeting of the Metropolitan New York Section to be held in the Military Park Hotel, Newark, N. J.

Corrosion of Iron and Steel was a talk given by C. P. Larrabee, U. S. Steel Corp., at the December meeting.

Kanawha Valley Section Nominates New Officers

Officers nominated at a recent meeting of the Kanawha Valley Section are:

Chairman: W. G. Mathews, Columbian Carbon Co., and G. F. Walther, Westvaco Chlor-Alkali Division.

Vice Chairman: K. R. Gosnell, Union Carbide Chemical Co., and Fred W. Lloyd, United Fuel Gas Co.

Secretary: C. P. Dillon, Union Carbide Chemical Co., and W. J. Foster, du Pont.

Treasurer: J. G. Brown, United Fuel Gas Co., and R. L. Davisson, Union Carbide Chemical Co.

Topic for the January 22 meeting will be Stress Corrosion of Stainless Steels, by Ken Bloom, Armco Steel. The meeting will be held in Charleston, W. Va.

Subject for the November meeting was Heat Exchanger Design Variables as They Affect Materials Selection, a talk by C. H. Gilmour of Union Carbide Chemical Co.

Southern New England

Corrosion problems in an electric power generating plant were discussed by Thomas McLaughlin, Hartford Electric Light Co., at the December meeting of the Southern New England Section held in Wallingford, Conn.

Officers nominated for 1959 are Chairman Archer B. Hamilton, Hartford Gas Co., Vice Chairman William W. Steinert, A. V. Smith Engineering Co., and Secretary-Treasurer Ralph O. Lewis, Charles Pfizer Co., Inc.

Auto Trim Test History Given at Boston Section

Efforts to develop an accelerated test correlated with actual breakdown of chrome plate on automobiles were discussed by Harold A. Kahler of General Motors at the Greater Boston Section November meeting.

After tracing the history of chrome trim from Duryea's polished brass in 1895 through Oldsmobile's nickel on brass in 1907, Mr. Kahler described the Detroit chrome tests conducted by GM. Test plates wired to taxicab bumpers indicated that chrome finish was more durable when applied on sound metal parts of known composition, when free from slivers and surface imperfections, when plated from controlled materials to close specifications, and when waxed after each wash job or wiped with light-grade motor oil to fill pores and small surface breaks.

Former tests were too long for practical purposes until Corrodcote, a ferric chloride paste, was used to approximate in only 48 hours the results of the older acetic acid test which lasted 192 hours. The CASS test (copper-accelerated salt spray) gives results in 16 hours equivalent to a year of Detroit service.

Mr. Kahler emphasized that no test will build quality into a part but that sound testing makes possible worthwhile prediction of part life and durability.

Future meetings of the section will be held January 14 with a talk on elastomeric coatings, March 11 with a talk on electrodeposited coatings and May 13 with a talk on water treatment.

Speaker From Israel Gives Talk on Cathodic Protection

Cathodic protection in Israel was the subject of a talk given by Dov Spector of Israel at the November International Meeting of the Baltimore-Washington Section.

With its agriculture dependent on irrigation, Israel has extensive waterworks and irrigation networks, according to Mr. Spector. The types of pipes used include steel, reinforced concrete and asbestos cement, all locally manufactured. Special corrosion problems are encountered with the reinforced concrete pipes which are the pre-stressed steel shell type, he stated.

Spector

Recently, national oil and product lines have been laid plus extensive communication and power cables requiring complex underground structures with the resultant corrosion problems.

Cathodic protection of small vessels has been used. Electrolytic descaling in sea water has been employed also.

The Technion (Israel Institute of Technology) has included cathodic protection courses in its regular curriculum. Two graduates have submitted theses on specific problems of cathodic protection.

President and chief engineer of his own consulting firm in Tel-Aviv, Mr. Spector is a member of NACE and internationally known for his technical papers and lectures.

Philadelphia Section Meets

The New Metals and Their Importance to the Corrosion Engineer was a talk given by Elbert M. Mahla, Dupont de Nemours & Co., Inc., at the Philadelphia Section's December meeting.

Western Region News

San Diego Section Plans Jan. 21 Meeting

Water borne corrosion will be the subject of a talk by Carl James, water consultant, to be given at the January 21 San Diego Section meetings at Lawton's Restaurant in La Mesa.

New officers will be installed.

Tony Codina was appointed chairman of the Library Committee at the November meeting to follow up a suggestion made that a corrosion section be set up in the San Diego City Library with contributions of books on corrosion and a complete file of CORROSION magazine by the section members.

Coal tar epoxy resin coatings were discussed by Tink Doyle, Magna Products, and Dick Whidden, Rocket Chemical Co.

Western Region To Install Officers

New Western Region officers will be installed at a joint meeting of the Western Region and the San Joaquin Valley Section to be held January 21 at Maison Jaussaud, 1001 South Union Avenue, Bakersfield, Cal.

The new officers are Chairman R. I. Stark, Vice Chairman A. E. Storm and Secretary-Treasurer R. L. Davis.

A social hour is scheduled at 6 pm with dinner at 7, followed by the technical program.

Color slides of the San Joaquin Valley Corrosion Tour held in September will be shown with questions and discussion by the members during the slide presentation.

Talk on Cathodic Circuits Planned at San Francisco

Circuit analogy in cathodic protection will be the topic of the January 14 meeting of the San Francisco Bay Area Section. Roy Dean of the Pacific Gas & Electric Company will give a talk entitled Equivalent Electrical Circuit Analogy of Structure-to-Soil Potentials.

Use of the corrosometer for refinery corrosion control was discussed by R. L. Piehl, Standard Oil of California, at the December meeting.

Portland Section Holds Meeting With Chemists

A joint meeting was held by the Portland NACE Section and the Portland Industrial Chemists Association for the Section's December meeting.

A talk on corrosion of underground piping was given by John Van Bladeren, Northwest Natural Gas Company; the operation and application of the corrosometer were discussed by Otto Hudrlik, the Flox Company.
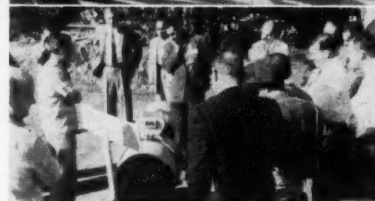
CORROSION CONTROL DEMONSTRATIONS like those shown above were included in the Western Region's 1958 Short Course held in November. Shown at top is a demonstration of soil resistance measurements. A practical demonstration of epoxy coatings is illustrated in the center photo. A test for coating holidays is shown in the bottom demonstration.

Western Region Conference Has Over 300 Registered

Over 300 people were registered at the 1958 Western Region Conference and Short Course held November 17-19 in Los Angeles, representing a 20 percent attendance increase over the 1957 Conference.

The short course was divided into four sections: cathodic protection, surface preparation for protective coatings, pipeline coatings and paint and plastic coatings.

Special merit award certificates were presented to Robert Kerr and Sid Galley for outstanding work in the region.

Educational Committee

An Educational Committee has been appointed by the Denver Section.

Committee chairman is Herbert L. Goodrich, American Telephone and Telegraph Co., Denver. Two other members appointed are Leonard W. Hartkemeier, Colorado School of Mines, Golden, and Henry Johns, Denver Federal Center's Bureau of Reclamation.

The committee was appointed by Section Chairman Paul W. Lewis, following recommendations by the South Central Region Board of Trustees.

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Members who register at the membership rate need to have their membership cards at the time they register.

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North Central Region News

INFORMAL DISCUSSIONS such as this one being held by Robert Zinn (left) of Vern E. Alden Co., Wendell Watkins (center) of Duriron Co., and I. J. Acosta (right) of the Crane Co., are considered helpful by Chicago Section members. Mr. Acosta is vice chairman of the section, which will be host to the NACE Annual Conference in March. The role of metallic coatings in corrosion control was discussed by David W. Levinson of the Armour Research Foundation at the section's November meeting.

University of Illinois Sets Dates for '59 Short Course

The fourth University of Illinois Biennial Short Course on Cathodic Protection will be held December 7-11 at the Urbana campus.

The Short Course is conducted by the Departments of Electrical Engineering and Mining and Metallurgical Engineering in cooperation with NACE.

Regional Officers Elected

North Central Regional officers recently elected are Chairman R. C. Weast of the Cleveland Section, Vice Chairman A. McConnell of the Eastern Wisconsin Section and Secretary C. W. Ambler.

SECTION CALENDAR

Jan.

6   Shreveport Section. Caddo Hotel. Fellowship hour, 6 p.m. Offshore Corrosion Control.
12 Central Oklahoma Section. At Youngblood Hotel, Enid. Fundamentals of Corrosion and Cathodic Protection, by Maurice A. Riordan, Rio Engineering Co., Houston.
14 Greater Boston Section. Elastomeric Coatings, by G. Carl Vogelsang, Gates Engineering Co.
14 Metropolitan New York Section. In Newark. Use of Epoxy Resins in Resistant Coatings, by H. W. Howard.
15 Vancouver Section. In B.C. Electric Bldg. Auditorium. Aluminum in Marine Environments, by T. J. Summerson, Kaiser Aluminum.
20 Chicago Section. Bacteria's Role in the Corrosion of Iron, by D. M. Updegraff, Minnesota Mining & Mfg., Co.
20 Cleveland Section. Cleveland Engineering and Scientific Center. Joint meeting with Electrochemical Society.
21 San Diego Section. At La Mesa. Water Borne Corrosion, by Carl James, water consultant.
22 Kanawha Valley Section. At Charleston, W. Va. Stress Corrosion of Stainless Steels, by Ken Bloom, Armco Steel.
26 Tulsa Section. Mayo Hotel.
26 Atlanta Section.
27 Panhandle Section.
27 Genesee Valley Section. Forum on Water Softeners.

Feb.

3   Shreveport Section. Caddo Hotel.
9   Central Oklahoma Section. At Avalon Cafeteria, Duncan. Testing Corrosion Inhibitors, by John A. Knox, Halliburton Oil Well Cementing Co.
10 Montreal Section. Hydrogen Attack on Steel, by W. Bonner.
17 Baltimore-Washington Section. Cathodic Protection Criteria, by W. J. Schwerdtfeger.
17 Cleveland Section. Cleveland Engineering and Scientific Center. Talk on linings.
17 Chicago Section. A Solution of Joint Electrolysis Problems in Stray Current Areas, by Louis Horvath, Ohio Bell Telephone Co.
18 Metropolitan New York Section. In New York City. High Temperature Corrosion, by E. N. Skinner.
24 Panhandle Section.
25 Genesee Valley Section. Results of Salt Test Corrosion Panel Placed on Automobiles.

All conference activities of the 1959 NACE Conference and Corrosion Show will be held in the Sherman Hotel, Chicago.

DEATHS

E. K. (Ted) Pierce died November 9. Vice-president of the Wm. Powell Company of Houston, he had been a NACE member since 1950.

James T. MacKenzie, who became a member of NACE on November 16, 1944, among the first to join, and who retained his membership until his death, died November 17. Dr. MacKenzie, formerly technical director of American Cast Iron Pipe Company and nationally recognized as an authority in the metallurgical field, retired April 6, 1956, after 44 years of continuous service with his company.

He was educated at the University of the South, Sewanee, Tennessee, and received honorary DSc degrees from this university and from University of Alabama.

E. F. Meier, chairman of NACE Unit Committee T-6H, died December 5. He was associated with Glascote Products, Inc., Cleveland. He was a 1922 mechanical engineering graduate of Oregon State College.

Teche Section Elects Stone as New Chairman

New officers for the Teche Section are Chairman John D. Stone, Sunray Mid-Continent Oil Co., Lafayette, La., Vice Chairman Sam E. Fairchild, Texas Pipe Line Co., Lafayette, Secretary Ron J. Cernick, Union Oil Company of California, Abbeville, La., and Treasurer Phil C. Brock, Dowell, Inc., Lafayette.

Stone

O. L. Bassham, Tretolite Co., Lafayette, continues as Section Trustee.

The officers will be installed at a dinner-dance meeting this month.

Bender to Be North Texas Section Chairman for '59

North Texas Section officers for 1959 are Chairman R. B. Bender, Tejas Plastic Material Supply Co., Ft. Worth; Vice Chairman Donald F. Taylor, Jr., Otis Engineering Corp., Dallas; Secretary-Treasurer Jerry R. McIntyre, Atlantic Refining Co., Dallas; and Section Trustee Glyn W. Beesly, Dallas Power & Light Co.

Microbes and Corrosion was the talk given by D. M. Updegraff, Minnesota Mining & Manufacturing Co., at the December meeting of the North Texas Section.

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Invitations to inspect the 1959 Corrosion Show in Chicago are obtainable from any of the exhibitors.

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The 1959 Corrosion Show is the fourth exhibition held by NACE in Chicago.

South Central Region News

Central Oklahoma Section Sets Dates

Meeting dates have been set for January, February and March by the Central Oklahoma Section.

Fundamentals of Corrosion and Cathodic Protection is the topic for the January 12 meeting to be held at the Youngblood Hotel in Enid. Speaker will be Maurice A. Riordan of Rio Engineering Co., Houston.

Topic for the February 9 meeting at the Avalon Cafeteria in Duncan will be Testing Corrosion Inhibitors. John A. Knox of Halliburton Oil Well Cementing Company is the speaker.

The March 9 meeting will be held at the Tropical Cafeteria in Oklahoma City.

New Section officers elected at the December meeting are Chairman George W. Evans, Southwestern Bell Telephone Co., Oklahoma City, Vice Chairman Frank B. Burns, General Asphalts, Inc., Wynnewood, Okla., and Secretary-Treasurer Truel E. Adams, Consolidated Gas Utilities Corp., Oklahoma City.

A talk entitled The NACE, Its Place in Industry and Your Place in It was given by J. C. Spalding, Jr., chairman of South Central Region, at the section's November meeting.

1963 Regional Meeting

Oklahoma City was designated as the site for the 1963 South Central Region conference. Announcement of the site was made by the Board of Trustees at the October regional meeting held in New Orleans.

Ashley Heads '59 Officers For Alamo Section

New officers for the Alamo Section are Chairman Leon Ashley, United Gas Pipe Line Co., San Antonio, Vice Chairman J. C. Kneuper, City Public Service Board, San Antonio, Secretary-Treasurer W. W. Elley, Southwestern Bell Telephone Co., San Antonio, and Trustee Max F. Schlather, United Gas Pipe Line Co., San Antonio.

Corrosion problems of buried pipes and the effect of grounding telephone lines to pipes were the topics for the Alamo Section's December meeting.

A motion picture entitled "All Holes Barred" was shown that dealt with corrosion control of buried steel pipes.

The effects of grounding telephone lines to pipes were discussed by Carl Thorn of Southwestern Bell Telephone Co.

Temporary rust preventives were discussed by Robert K. Johnston, Southwest Research Institute, at the November meeting of the Alamo Section held in San Antonio.

Shreveport Section Elects Wise as New Chairman

Shreveport Section officers elected for 1959 are Chairman John J. Wise, Vice Chairman R. P. Naremore, Secretary Grady Howell, Treasurer D. F. Tefankjian and Trustee E. H. Sullivan.

Section meetings are scheduled for the first Tuesday of each month at the Caddo Hotel in Shreveport.

A talk on Corrosion Control of Gas Wells by Concentric Completions was given by Leroy DeRouen, Union Oil & Gas Corp., Lake Charles, at the December meeting of the Shreveport Section.

Offshore corrosion control will be the technical subject for the section meeting to be held in the Caddo Hotel on January 6.

Corpus Christi Section

Talks on cathodic protection and tape coating were given at the November meeting of the Corpus Christi Section.

Basic Principles of Cathodic Protection as Applied to Well Casings was given by Hugh Wilbanks, Jr., and Application of Protective Tape Coating was the subject of a talk by John McIntosh. Both men are affiliated with Cathodic Protection Service, Corpus Christi.

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Over 100 companies will have exhibits in 140 booths at the 1959 Corrosion Show in Chicago, March 17-19.

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Invitations to inspect the 1959 Corrosion Show in Chicago are obtainable from any of the exhibitors.

Corrosion Control by Use of Sprayed Metal Discussed at Houston Section Meeting

Uses of sprayed metal to prevent corrosion were presented to the Houston Section at the November meeting by S. John Oechsle, Jr., executive vice-president, protective coatings division, Metalweld, Inc., Philadelphia.

In a discussion after his talk, Mr. Oechsle admitted that the potential and projected performance of metal spraying has not been fully explored. He stressed the importance of cooperative effort of corrosion engineers in developing standards and specifications for metals spraying as is done for other methods of corrosion prevention. He stated that NACE in this and other ways has something of great value to sell to management.

He indicated that NACE members tend to underestimate the association's value. He urged corrosion engineers to keep top level executives informed of the economic consequences of corrosion damage and of the savings corrosion control makes possible. Properly approached management will provide funds for NACE in volume, he believes.

Four principal uses of metallizing described by Mr. Oechsle are machine element metallizing, corrosion contamination prevention, combination coatings and high-temperature coatings.

In machine element metallizing, worn parts are built up by spraying a thin, wear-resistant coating of high-cost metal on shafts and other wearing parts. With only a thin coating of expensive metal sprayed on a cheaper metal, total cost of the part is drastically reduced but performance is unaffected. Stainless steel, nickel, Monel or aluminum can be sprayed on carbon steel in desired areas. The sprayed coating is porous and retains lubricants.

Zinc and aluminum sprayed on steel equipment affords cathodic protection and reduces the possibility of iron oxide contaminating the product. Only warm, fresh water is required to clean surfaces thus protected. Cathodic action during cleaning prevents rust from forming. Organic liquids can be protected from contamination by spraying vessels with stainless steel or other metal coatings, provided the product will not attack the base metal or coating. When the product comes into contact with the base metal through the porous metal coating, it polymerizes within the structure of the sprayed metal, Mr. Oechsle said.

Combination coatings supplement each other, he stated. Coal barges on the Delaware River were sprayed with zinc and sealed with a marine paint. The combination proved so successful that inspections were necessary every two years instead of yearly. Only touch-up work has been needed where ice and other mechanical abrasion has damaged the coating. After 20 years there is no loss of steel or corrosion on the barges.

Sprayed metal has been used as protection at temperatures up to 1800 F. One process involves the application of a sprayed aluminum coating, the addition of a special paint-type sealer and subsequent heat treatment of the coated part. Protection against combined heat and corrosion is provided by the absorbed layer of aluminum.

Newer developments in sprayed powder coatings were also described. New powder guns for spraying of alloy and ceramic have a deposit efficiency above 90 percent, and sufficient heat can be applied for spraying the high melting point materials like alumina and zirconia. Three basic groups into which materials can be divided when used in a powder gun are self-fluxing alloys, oxidation resistant alloys and ceramims.

Good surface preparation is a necessity for good metal spraying. Angular steel grit is preferable where the grit can be recovered. Crushed chat is good when a type is selected which will not leave tiny particles imbedded in the surface. The best way to obtain a good metal spray job is to deal with well-established contractors with good reputations and proven ability. Some major companies use restricted bid lists and will not consider a bid from any unlisted contractor, Mr. Oechsle said.

To show how important the corrosion problem is to some companies, Mr. Oechsle called attention to reprints from a technical publication he had distributed at the meeting, telling of how Dow Chemical Company's Texas Division tests corrosiveness of atmospheres in more than 150 different locations in its Freeport installations. The company spends more than one million dollars yearly on its paint maintenance program.

Baton Rouge Officers

New officers for the Greater Baton Rouge Area Section are Chairman A. H. Tuthill, Vice Chairman Donald C. Townsend and Secretary-Treasurer W. E. Doescher, Jr.

At the December section meeting, a talk on Plastics in Corrosion Service was given.

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Latest developments in processes, materials, methods, processes and equipment for corrosion control will be on display at the 1959 Corrosion Show.

W. S. SPANGLER, center, vice president and general manager of Humble Pipe Line Co., receives congratulations from O. A. Melvin, Carboline Co., secretary-treasurer of the Houston Section after Mr. Spangler's address to the December section meeting. At right is A. B. Campbell, former executive secretary of NACE who also participated in the program. Mr. Spangler spoke on corporate membership.

New Officers Installed By East Texas Section

New officers installed at the December meeting of the East Texas Section are Chairman W. R. Carrol, Humble Oil Co., Vice Chairman J. R. Richards, Tidewater Oil Co., Secretary Ike Hartsell, Tretolite Co., Treasurer Gene Smith, Lone Star Steel and Educational Secretary J. N. Graves, Tidal Pipeline Co.

Organic Chloride Contamination of Crude Oil and Its Effect on Platforming was a talk by Charles Petty, La Gloria Corp., at the November meeting of the East Texas Section held in Longview.

Teche Short Course Dates

Dates for the Teche Section Corrosion Control Short Course have been set for June 2-4.

The course was scheduled in the middle of the week to allow for travel time on Monday and Friday.

The course will be held at Southwestern Louisiana Institute, Lafayette.

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South Central Region Meeting has been set for October 12-15 in Denver.

SOME OF THE REGISTRANTS at the November Florida General Conference held in Miami are shown above. Over 100 were registered. At the left are (left to right) J. B. Prine, Jr., conference director, Colonel J. D. Sams, one of the conference speakers and Harry T. Truchlet, member of the Conference Financial Committee. The conference was sponsored by the Miami and Jacksonville Sections.

Carolinas Section Meets

Corrosion Aspects of Aluminum was a talk given by J. B. West, Aluminum Company of America, at the December meeting of the Carolinas Section.

L. S. Bake of du Pont spoke on the use of elastomeric coatings.

NATIONAL and REGIONAL MEETINGS and SHORT COURSES

1959

Jan. 12-14—Canadian Region. Sheraton Mount Royal Hotel, Montreal, Quebec.

Feb. 11-13—Canadian Region. Calgary, Alberta.

March 16-20—15th Annual Conference and 1959 Corrosion Show. Sherman Hotel, Chicago.

Sept. 29-30, Oct. 1—Western Region Conference. Bakersfield Inn, Bakersfield, Cal.

Oct. 1-2—Southeast Region. Jacksonville, Florida.

Oct. 5-7—Northeast Region. Lord Baltimore Hotel, Baltimore, Md.

Oct. 12-15—South Central Region Meeting, Denver, Col. Cosmopolitan Hotel.

Oct. 20-22—North Central Region, Cleveland.

1960

March—16th Annual Conference and 1960 Corrosion Show. Dallas, Texas, Memorial Auditorium.

Oct. 11-14—Northeast Region Meeting. Huntington, W. Va.

Oct. 19-20—North Central Region. Milwaukee.

Oct. 25-28—South Central Region Conference, Mayo Hotel, Tulsa.

1961

March—17th Annual Conference and 1961 Corrosion Show. Buffalo, N. Y., Hotel Statler.

Oct. 24-27—South Central Region Conference, Houston, Shamrock Hotel.

1962

March—18th Annual Conference and 1962 Corrosion Show. Kansas City, Municipal Auditorium.

October 16-19—South Central Region Conference, San Antonio, Texas.

SHORT COURSES

1959

January 22-23. Houston Section. Short Course on Fundamentals of Corrosion Control. University of Houston, Oberholtzer Hall.

February 11-13—Tulsa Section. Tenth Annual Pipe Line Short Course. Mayo Hotel.

March 31-April 12. Corrosion Control Short Course. University of Oklahoma-Central Oklahoma Section. North Campus, University of Oklahoma, Norman.

June 2-4—Teche Section. Corrosion Control Short Course.

December 7-11—University of Illinois Biennial Short Course on Cathodic Protection. Urbana Campus.

Aircraft Turbine Corrosion Discussed by Ohio Section

Corrosion of Aircraft Gas Turbine Materials by Combustion Products of High Energy Fuels was the title of a talk given by William Spurgeon of General Electric at the November meeting of the Southwestern Ohio Section.

Test methods were outlined and test samples were shown of various metals used to study the effect of temperature on corrosion activity.

15th ANNUAL CONFERENCE
and
1959 Corrosion Show

NATIONAL ASSOCIATION of CORROSION ENGINEERS

90 Technical Papers to Be Given in 16 Symposia

A wide diversity of corrosion control problems in industry will be covered in the 90 papers to be presented in the 16 symposia and two round table discussions scheduled for the NACE 15th Annual Conference and Corrosion Show in Chicago's Hotel Sherman, March 16-20.

Registrants will be able to see corrosion control methods, equipment, materials and processes at the 110 booths set up by about 85 companies at the Corrosion Show.

The 90 symposia papers are by over 120 authors employed by 58 companies from diverse fields ranging from atomic power research to pharmaceuticals. Electric manufacturing, plastics and paper industries are included among numerous others.

A tabulation showing the number of companies employing authors in each of these fields is given below:

Field	No.
Atomic Power Research	3
Cathodic Protection	2
Chemicals	10
Coatings	4
Electric Manufacturers	3
Metal Fabricators	3
Metal Producers	2
Mining and Smelting	1
Non-metallic Producers	3
Paper Producers	1
Petroleum	7
Pharmaceutical Manufacturers	1
Pipelines	1
Plastics Manufacturers	2
Processing Equipment Manufacturers	3
Refinery Construction	1
Research and Engineering	11

General Business Meeting

The General Business Meeting for the Chicago Conference is scheduled for 11 am on Wednesday, March 18. No symposia or technical committees will meet at this hour.

Reports of standing committees of NACE are to be given, and actions of the Board of Directors for the year will be presented to the membership for approval.

The officers also will make reports on the work of the association.

Cathodic Protection

4 Papers

Wed., March 18

2-5 pm

Protection for Pipe Lines and Offshore Platforms to Be Covered

Four papers in the Cathodic Protection Symposium pertain to protection of pipe lines in manufacturing plants, of offshore platforms and internal protection of salt water mains.

One paper presents new developments in cathodic protection rectifiers.

Educational Lectures and Corrosion Principles Included In 16 Conference Symposia

Two roundtable discussions and two additional symposia are included in the NACE Annual Conference in Chicago.

The Corrosion Principles Symposium will meet 8:30-11 am, Wednesday, March 18. Co-chairmen are Frederick W. Fink, Battelle Memorial Institute, and W. S. Quimby, Texas Company.

Theme of the Educational Lectures Symposium will be the effects of radiation on corrosion. Papers will be presented by H. H. Uhlig, MIT, G. H. Jenks, Oak Ridge National Laboratory, and M. T. Simnad, General Atomic.

The roundtable discussion on General Corrosion Problems will be held Friday, March 20, 9-12 am. Chairman is T. P. May, International Nickel Co., Wrightsville, Beach, N. C. A business reply card is being mailed to all members for questions to be submitted for consideration at this roundtable.

Also included in this mailing to all members will be an advance program, registration material and hotel reservation cards.

Chairman for the Pipe Line and Underground Corrosion Roundtable scheduled for 9-12 am, Friday, March 20, is E. R. Allen, Jr., Humble Pipe Line Co., Houston.

Entertainment Planned For Banquet and Dance

Entertainment for the Chicago Conference banquet and dance on Wednesday, March 18, will include a dance team, singing stars, a master of ceremonies and an orchestra.

Master of ceremonies for the banquet entertainment will be Nip Nelson, Radio City Music Hall star. Jackie Van, star of her own TV show on Mutual Broadcasting System, will be feature vocalist.

The Lenore Sutton Dancers, recently booked at the Palace Theater in New York and the Benny Meroff and Kathleen McLaughlen duo-act will be included in the banquet show.

Music for the banquet and dance will be furnished by Marty Gould and his 15-piece Chez Paree Orchestra.

Chairman of the Entertainment Committee is P. E. Henneberry.

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The 1959 Corrosion Show is the fourth exhibition held by NACE in Chicago.

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Latest developments in processes, materials, methods, processes and equipment for corrosion control will be on display at the 1959 Corrosion Show.

A B S T R A C T S

Internal Cathodic Protection of Salt Water Mains by W. B. Clary and R. D. Merrick, Esso Research and Engineering Company, Linden, N. J.
Feasibility of using an impressed current cathodic protection system to prevent internal corrosion of salt water mains was demonstrated by extensive pilot scale tests. Current distribution, anode spacing and curent densities required under flow conditions based on these tests are discussed.

Advantage of cathodic protection is its reliability and in-service checking of protection. An impressed current system is preferred to galvanic anodes because a 100 percent service factor is required for refinery salt water mains. The economics of the impressed current system compared to other protective systems is presented.

Two commercial applications of an impressed current system to salt water mains are discussed.

Cathodic Protection of Offshore Platforms by Wayne A. Johnson and James T. Condry, Corrosion Rectifying Co., Houston.
The type, areas and degree of corrosion prevalent on offshore platforms are explained. Methods of determining the corrosion rate are also given. Rectifier-graphite anode systems and galvanic anode systems are described, and cost figures for each are compared. Good and bad features of present systems are discussed with future developments.

New Developments in Cathodic Protection Rectifiers by Harry R. Aschan, Good-All Electric Mfg. Co., Ogallala, Nebraska.
Development is discussed of high voltage selenium and silicon rectifying elements and the use of these elements in circuits which are new to cathodic protection. Other changes in recitifier materials and designs are given also.

Variations in rectifier types such as small oil immersed units have resulted in better distribution factors and less interference by means of distributed ground bed systems.

Advances in control of rectifier output are discussed.

Cathodic Protection of Underground Pipe Lines in Manufacturing Plants by B. Husock, Harco Corp., Cleveland, Ohio.
A method of determining the corrosion pattern on underground plant piping is described. The quantities which must be considered in the design of a cathodic protection system are also given. Techniques and instrumentation for field measurements are outlined.

Women's Entertainment Program Is Planned

Women attending the Chicago Conference will be entertained Tuesday, March 17 at the Martha Logan Kitchens. The Ladies' Program Committee consists of Mds. Ann Janota, L. Risetter, M. Fletcher and R. McFarland.
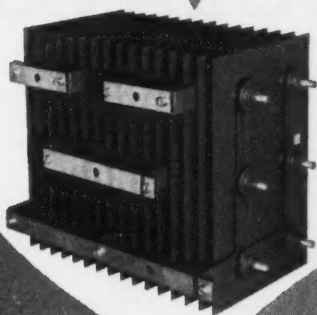
A hat style show is scheduled for the women on Wednesday, March 18, featuring Miss Lee Phillips, CBS-TV star.

Additional entertainment is being planned for Thursday, March 19.

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All conference activities of the 1959 NACE Conference and Corrosion Show will be held in the Sherman Hotel, Chicago.

Chemical Industry

Titanium, Zirconium Uses Among Topics of Eight Presentations

Uses of titanium, zirconium, Hortonclad and glass steel for corrosion control are subjects included in the eight papers for the Chemical Industry Symposium. Two sessions are scheduled.

Other subjects include the use of glass cloth and epoxy resins for external protection of glass lined vessels, relation of accumulative residues on material selection and application, design and materials for reduced pump corrosion and roofing maintenance in the chemical industry. Another paper discusses the corrosion problems of an equipment manufacturer.

6 Papers

Session One

Tues., March 17

9-12 am

Session Two

Wed., March 18

2-5 pm

Conference Chairmen Listed for Chicago

General Chairman for the 1959 NACE Chicago Conference is Rudolph B. Janota, Swift & Co., Chicago. Other conference committee chairmen are listed below:

Technical Program: Rolland McFarland, Jr., Hills-McCanna Co., Chicago. Co-chairman is S. K. Coburn, Association of American Railroads, Chicago.

Exhibition: W. H. Schultz, Dearborn Chemical Co., Chicago.

Publicity: L. V. Collings, Sinclair Research Laboratories, Harvey, Ill.

Local Arrangements and Program Coordinating: D. B. Sheldahl, Sinclair Research Lab., Harvey, Ill. and Richard Rue, Insulmastic Corp., Summit, Ill., co-chairmen.

Registration: J. J. Irwin, Revere Chemical Co., Chicago.

Ladies' Program: Mdms. R. B. Janota, E. Risetter, M. Fletcher and R. McFarland.

ABSTRACTS

Accumulative Residues—Their Relation to Material Selection and Equipment by Harry Gilman, General Aniline and Film Corp., Linden, N. J.

The corrosion engineer can reduce the failures of boilers, turbines and other equipment caused by clogging of deposits and residues by programming additional material testing for residues and their origin. In many cases a change in the material prior to design and fabrication will eliminate this problem, or at least improve or minimize maintenance. A case history in a large distilling column is discussed, relating the type and cost of equipment, the accumulative residues and their effect on the surfaces.

Roofing Maintenance in the Chemical Industry by W. G. Craig, Lubrizol, Wickliffe, Ohio, and J. C. Lemmon, Roofing Consultants, Inc.

Types of roofing construction encountered are discussed with emphasis on the types of conventional roofing and waterproofing during initial construction. Limitations of construction and surfacing methods are given in detail. Various maintenance methods, materials and application are explained with comparative costs. Problems of roofing in the chemical industry are discussed with possible corrective materials and methods given.

Design and Materials for Reduced Pump Corrosion by Jack E. Piccardo, Dorr-Oliver Inc., Oakland, Cal.

Requirements of pumps in the chemical and allied industries are discussed: to handle corrosive liquids under conditions of high pressure and high temperature, corrosive liquids which may be radioactive, expensive or hazardous liquids and liquids with solids in suspension often of an abrasive nature.

Design features to solve these problems are presented: improved sealing devices where the pump shaft passes through the casing, new alloys or metals for the wetted end which will provide a greater degree of corrosion resistance and improved elastomers, plastics and ceramics which will permit the pump to be lined to provide a high degree of corrosion resistance.

Corrosion Resistance of Titanium and Zirconium in Chemical Plant Exposures by W. Wilson and P. J. Gegner, Columbia-Southern Chemical Corp., Barberton, Ohio.

Titanium was found to have low corrosion rates in such varied exposures as wet chlorine gas, sodium hypochlorite, calcium hypochlorite, hypochlorous acid, nitric acid, calcium chloride, sodium chloride, sodium hydroxide and chlorine-saturated solutions of sulfuric acid, water, sea water and brine.

Zirconium was found to have excellent resistance to nitric acid and related exposures, sodium hydroxide, hydrochloric acid, dry chlorine, sodium hypochlorite, calcium chloride, sodium chloride and some chlorine saturated solutions of sulfuric acid.

Corrosion Characteristics and Uses of Glassed Steel by David Kenneth Priest, Pfaudler-Permutit, Inc., Rochester, N. Y.

Corrosion behavior of glass steel is contrasted with metallic corrosion. Problems concerning galvanic attack, concentration cells, chlorides and electrochemical reactions in general are shown to be non-existent in glass steel.

The mechanisms and characteristics of corrosion which are important in relation to glass steel are discussed. All acids except hydrofluoric and hot, concentrated phosphoric can be contained in glass steel at temperatures to 300 F and often to higher temperatures. Resistance to alkalis is lower, but solutions to pH 12 at 212 F can be handled. Corrosion resistance to pure water is limited at temperatures above 200 F unless environment is modified.

Areas of usefulness in the chemical, pharmaceutical and other industries are outlined. Examples of successful applications of glassed steel solving corrosion and other problems are given.

Use of Glass Cloth and Epoxy Resins for External Surface Protection of Glass Lined Vessels by George H. Herman, Parke, Davis and Co., Detroit.

A method is described using glass cloth and epoxy resins to reduce maintenance costs of chemical equipment in high corrosive areas. These materials are applied directly to the exterior of glass-lined vessels after suitable surface preparation. Epoxy enamels of desired color standards are applied as a finish coat.

Chicago Papers to Be Considered for Publication

Papers presented at the Chicago Conference will be considered for publication in CORROSION after review by the NACE Editorial Review Sub-Committee and approval by the editor of CORROSION. This process, though sometimes lengthy, results in the publication of technical information which is as accurate and complete as expert reviewers can make it.

Publication in CORROSION assures authors their papers will be abstracted in NACE abstract services and completely and correctly indexed in CORROSION's annual and multiple-year indexes.

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All conference activities of the 1959 NACE Conference and Corrosion Show will be held in the Sherman Hotel, Chicago.

Technical Committees—Tentative Schedule of Meetings

Monday March 16	A.M.	T-1	T-2C	T-2J	T-5A-1 T-5A-3 T-5A-6	T-6G	T 2B	T-6H	
	P.M.		T-3G-1	T-5A-4 T-5A-5 T-5A	T-4F-1 T-4F	T-3H	T 2G		
Tuesday March 17	A.M.		T-4B-6 T-4B-1 T-4B-2	T-3G	T-3F	T-2E	T-3C	T-2D	
	P.M.		T-4B-3 T-4B-5 T-4B-4	T-4E					
Wednesday March 18	A.M.	T-8A	T-6A	T-5D	T-2H	T-5B	T-1D T-1H	T-3D	T-2K	T-2A
	P.M.	T-8	T-7B T-7	T-6B	T-1B T-1C	T-4A	T-3A T-3B	T-6R	T-2L
Thursday March 19	A.M.		T-6E	T-6K	T-3E	T-6F	T-6C		ISCC
	P.M.	T-8	T-1K T-1M	T-5E (2-4pm)	T-6D (2-4pm)	T-1F T-1F-1 T-1F-2	T-4D (2-4pm)		

REPRINTS
Of Articles Published In Corrosion

Remittances must accompany all orders for literature the aggregate cost of which is less than $5. Orders of value greater than $5 will be invoiced if requested. Add 65c per package to the prices given below for Book Post Registry to all addresses outside the United States, Canada and Mexico. Send orders and remittances to NACE, 1061 M&M Bldg., Houston 2, Texas.

Aluminum

The Performance of Alcan 65S-T6 Aluminum Alloy Embedded in Certain Woods Under Marine Conditions by T. E. Wright, H. P. Godard and I. H. Jenks 50

Application of Statistical Theory of Extreme Values for the Analysis of Maximum Pit Depth Data for Aluminum by R. M. Aziz 50

The Corrosion Behavior of Aluminum by Hugh P. Godard 50

Aqueous Corrosion of Aluminum—Part 2—Methods of Protection Above 200 C by J. E. Draley and W. E. Ruther 50

Compatibility of Aluminum With Alkaline Building Products by C. J. Walton, F. L. McGeary and E. T. Englehart 50

Structural Features of Corrosion of Aluminum Alloys in Water at 300 C by Kurt M. Carlsen 50

The Static Electrode Potential Behavior of Aluminum and the Anodic Behavior of the Pure Metal and Its Alloys in Chloride Media by E. M. Khairy and M. Kamal Hussein 50

Reaction of Certain Chlorinated Hydrocarbons with Aluminum by A. C. Hampstead, G. B. Elder and J. C. Canterbury 50

Effects of Cold Working on Corrosion of High Purity Aluminum in Water at High Temperatures by M. J. Lavigne 50

Cathodic Protection and Pipe Lines

Cathodic Protection of Internals of Ships by L. P. Sudrabin 50

Cathodic Protection of Oil Well Casings at Kettleman Hills, California by J. K. Ballou and F. W. Schremp 50

Cathodic Protection of an Active Using Zinc Anodes by B. H. Tytell and H. S. Preiser . .50

The Application of Cable in Cathodic Protection—Part I by M. A. Riordan and Part II by R. G. Fisher 50

Economic Considerations in Pipe Line Corrosion Control by L. G. Sharpe 50

Application of Cathodic Protection to 48 Well Casings and Associated Production Facilities at Waskom Field by G. L. Doremus, W. W. Mach and J. J. Lawnick . .50

Potential Criteria for the Cathodic Protection of Lead Cable Sheath by K. G. Compton 50

Use of Graphite as Duct Anodes by A. L. Ayres 50

Lead Cable Sheath Corrosion Under Cathodic Protection Conditions by Walter H. Bruckner and Ray M. Wainwright . . .50

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Some Experiences with Sodium Silicate as a Corrosion Inhibitor in Industrial Cooling Waters by J. W. Wood, J. S. Beecher and P. S. Laurence 50

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Inhibiting Effect of Hydrofluoric Acid in Fuming Nitric Acid by David M. Mason, Lois L. Taylor and John B. Rittenhouse . .50

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Corrosion and Metal Transport in Fused Sodium Hydroxide (Part 2—Corrosion of Nickel-Molybdenum-Iron Alloys) by G. Pedro Smith and Eugene E. Hoffman 50

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The Growth of Ferrous Sulfide on Iron, by R. A. Jeussner and C. E. Birchenall 50

Standardization in the Field on Corrosion and Corrosion-Protection in Germany by Henry Hives 50

A Kinetic Study of Acid Corrosion of Cadmium by Henry Weaver, Jr. and Cecil C. Lynch 50

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SYMPOSIUM ON CORROSION BY HIGH PURITY WATER

Introduction, John F. Eckel

Corrosion of Structural Materials, A. H. Roebuck, C. R. Breden and S. Greenburg.

Corrosion Engineering Problems, D. J. DePaul.

Importance of Data to Industrial Application. W. Z. Friend. Per Copy $1.50

The Corrosion of Iron in High-Temperature Water. Part I—Corrosion Rate Measurements by D. L. Douglas and F. C. Zyzes . . .50

Corrosion Studies in High Temperature Water by a Hydrogen Effusion Method by M. C. Bloom, Krulfeld, W. A. Fraser and Vlannes 50

The Corrosion of Steel in a Reinforced Concrete Bridge by R. F. Stratfull 50

The Oxidation of Molybdenum by E. S. Jones, Capt. J. F. Mosher, Rudolph Speiser and J. W. Spretnak 50

A Kinetic Study of Acid Corrosion of Cadmium by Henry Weaver, Jr. and C. C. Lunch 50

Corrosion of Metals in Tropical Environments. Part 1—Five Non-Ferrous Metals and a Structural Steel, by B. W. Forgeson, C. R. Southwell, A. L. Alexander, H. W. Mundt and L. J. Thompson 50

Prevention of Localized Corrosion in Sulfuric Acid Handling Equipment by G. A. Nelson 50

High Temperature Oxidation of Iron-Nickel Alloys by M. J. Brabers and C. E. Birchenall 50

Controlling Corrosion in Coal-Chemical Plants by C. P. Larrabee and W. L. Mathay 50

Corrosion and the Destination of Corrosion Products in a High Pressure Power Plant by Ross C. Tucker 50

Methods for Increasing the Corrosion Resistance of Metal Alloys by N. D. Tomashov 50

Corrosion of Zinc by Differential Aeration by G. Bianchi .50

Petroleum Production and Storage

Naphthenic Acid Corrosion—An Old Enemy of the Petroleum Industry by W. A. Derungs 50

Analysis of Corrosion Pitting by Extreme Value Statistics and Its Application to Oil Well Tubing Caliper Surveys by G. C. Eldredge 50

Interpretation of Tubing Caliper Surveys by Victor W. Maxwell and Ben D. Park 50

A Laboratory Study of N-Oleoyl Sarcosine as a Rust Inhibitor in Some Petroleum Products by Robert M. Pines and John D. Spivack 50

Sulfide Corrosion Cracking of High Strength Bolting Materials by Donald Warren and G. W. Beckman 50

Corrosion in Amine Gas Treating Solutions by F. S. Lang and J. F. Mason, Jr. 50

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THREE PAPERS ON SULFIDE CORROSION

A Note on the Value of Ammonia Treatment for Tank and Casing Annulus Corrosion by Hydrogen Sulfide by Walter F. Rogers

Use of Ammonia to Prevent Casing Corrosion by H. E. Greenwell, Rado Loncaric and Harry G. Byars

Electrochemical Studies of the Hydrogen Sulfide Corrosion Mechanism by Scott P. Ewing 1.00

Stainless Steel, Titanium

The Effect of No, HNO₂, and HNO₃ on Corrosion of Stainless Steel by H₂SO₄ by W. P. McKinnell, Jr., L. F. Lockwild, R. Speiser, F. H. Beck and N. G. Fontana . .50

Inhibiting Effect of Hydrofluoric Acid in Fuming Nitric Acid on Corrosion of Austenitic Chromium-Nickel Steels, by Clarence Levoe, Davi dMason and John Rittenhouse 50

Corrosion Inhibitors

4 Papers

Wed., March 18

8:30-11 am

Corrosion in High Flux Reactors One of Three Symposia Topics

Three papers in the Corrosion Inhibitors Symposium cover magnesium alloy applications in a high flux research reactor to reduce high temperature corrosion, use of fatty nitrogen chemicals as corrosion inhibitors for oil-water systems, mineral-acid systems, secondary oil recovery and other applications, and a study of nonylphenoxyacetic acid as an inhibitor for ferrous metals in a variety of petroleum fluids.

Corrosion Show's Main Feature Is Diversification

What promises to be the most widely diversified display of corrosion control materials, equipment and processes so far shown at an NACE conference is indicated for the 1959 Corrosion Show. The show, to be held concurrently with the NACE 15th Annual Conference at Hotel Sherman, will be open March 17-19. The exhibit area is in the hotel, where all technical, business and social events will be held.

At the end of 1958, a total of 88 exhibitors had contracted for 113 booths. R. J. Huff, Jr., NACE assistant executive secretary, who is in charge of the exhibit, estimated that all of the projected 140 booths would be contracted for by the time the exhibit opens.

A survey of the equipment and materials exhibitors indicate they will have on display supports a forecast that a greater variety of exhibits will be available than for former NACE exhibitions. Many companies that have not exhibited previously at NACE shows have signed for space.

In addition to the companies listed in October and December, the following will have exhibits:

H. B. Reed & Co., Inc.
Royston Laboratories, Inc.
Armour Chemical Division
Koppers Co., Inc.
Good-All Electric Mfg. Co.
Centriline Corporation
Pittsburgh Corning Corp.
Charleston Rubber Co.
Solvay Process Division,
    Allied Chemical Corp.

Speller Award to Be Made At Conference Banquet

The Speller award, given annually by NACE to an outstanding corrosion engineer will be made on the evening of March 18 at the association's annual banquet. Only the Speller award will be made this year.

The author of a technical paper published in CORROSION who is less than 30 years of age also is honored at the banquet. The most meritorious paper is selected by the Young Author Award Committee, and the author or authors are given a small honorarium. The fund from which the honorarium is taken was given anonymously to the association.

Honorees for the Whitney and Speller awards are selected by an awards committee headed by the immediate past president of NACE.

5 Regional Meetings Scheduled for Fall '59

Five meetings of NACE regions have been scheduled for the fall of this year. The meetings begin September 29 and run almost continuously through October 22. No requests have been made for exhibitions to be held in connection with any region meeting. South Central Region, which has held exhibitions concurrently with its annual meeting for three years, will not sponsor an exhibition in 1959.

These will bring to six the number of regional meetings held by NACE in 1959. The Canadian Region is having its eastern division meeting at Montreal in January and its western division meeting at Calgary in February.

NACE regional meetings usually are oriented to the industrial interests of the region in which they are held. This permits attention to many corrosion problems which cannot be covered completely at national meetings, and frequently makes possible programs cast at a different level than those at national conferences.

Persons who are interested in the regional meetings may find a list of dates and places under the heading "National and Regional Meetings and Short Courses" in CORROSION's NACE News section. News about the meetings and their programs will be published as it becomes available.

Corrosion Exhibit Planned At 1960 NACE Meeting

A corrosion show will be held concurrently with the 16th Annual NACE Conference scheduled to be held at the Dallas Memorial Auditorium in March, 1960. This is one of four shows scheduled to be held annually through 1963.

Other shows will be held at Buffalo, Kansas City and Philadelphia.

15th Conference
Hotel Sherman
March 15-20
Registration Hours
Sunday, 1-5 pm
Monday, 8 am-4 pm
Tuesday, 8 am-4 pm
Wednesday, 9 am-4 pm
Thursday, 9 am-4 pm
Friday, 9-11 am

A B S T R A C T S

Corrosion Control With Fatty Nitrogen Derivatives by B. E. Marsh, Armour Chemical Division, Chicago.
Use of fatty nitrogen chemicals as corrosion inhibitors for oil-water systems, mineral-acid systems, secondary oil recovery and other applications is discussed. Methods of evaluation are briefly covered, including a simple oil wetting test which is a possible rapid screening method for chemicals as corrosion inhibitors in oil-water systems.

Fatty diamines appear most effective in this evaluation. Quaternaries were found to be the most effective chemicals in sulfuric acid systems; amines and reaction products thereof were the most effective in hydrochloric acid systems.

Aqueous Corrosion of Magnesium Alloys at 150 C by S. Greenberg and W. E. Ruther, Argonne National Laboratory, Lemont, Ill.
Magnesium is a possible fuel cladding material for nuclear reactors because of its low thermal neutron absortion cross section but corrodes rapidly in water at high temperatures. The most corrosion resistant commercial allow suitable for reactor use, AZ 31, corrodes at 3.3 mils per day in distilled water at 150 C.

A maximum rate of 1 mil per day was specified for use in a proposed high flux research reactor. At 150 C, corrosion was reduced to about 1.5 mils per day by including a copper cathodic element such as 5 Al-1 Sn or 1 Zn-0.5 Cu. in AZ 31 composition. Fluoride ion in the concentration range of 1 to 100 ppm reduced corrosion of commercial and experimental alloys to 1 mil per day. Combining fluoride treatment with control of pH in the 6 to 7 range reduced corrosion of AZ 31 and the experimental alloys 0.1 to 0.2 mils per day at 150 C. Except for fluoride, the inhibitors commonly effective at room temperature were ineffective at 150 C.

A Laboratory Study of the Rust Preventive Properties of Nonylphenoxyacetic Acid in Some Petroleum Products by Robert M. Pines and John D. Spivack, Geigy Chemical Corp., Ardsley, N. Y.
Nonylphenoxyacetic acid is an effective corrosion inhibitor for ferrous metals in a variety of petroleum based fluids. Tests indicate its suitability in lubricants, hydraulic and preservative oils, cutting fluids, gasoline and jet fuels. It is also an effective rust inhibitor in synthetic lubricants such as the silicones. The water soluble alkali metal or amine salts are good inhibitors in aqueous systems. The compound also has versatility, compatability with hydrocarbon liquids and excellent inhibiting properties.

The Use of Sodium Molybdate as a Corrosion Inhibitor for Mild Steel and Cast Iron in Aqueous Solutions by George W. Lewis, Jr., Climax Molybdenum Co., Detroit.

Some Papers Considered For Technical Topics

Some of the technical papers presented at the Chicago meeting may be selected for publication in the Technical Topics section of CORROSION. This section includes material considered to be of immediate applicatory nature.

A paper selected for this section may be revised or abbreviated but usually is published sooner than papers which are sent to the NACE editorial review subcommittee. Authors are given an opportunity to review revisions before publication.

Papers for this section also are accepted without invitation.

January,

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Elevated Temperature

**9 Papers
Session One
Wed., March 18
8:30-11 am
Session Two
Thurs., March 19
9-12 am**

Corrosion to Publish Technical Discussions

Discussions presented after delivery of technical papers are solicited for publication in CORROSION. Persons who discuss papers are urged to fill out a discussion record form, giving the information required.

NACE Central Office will solicit discussions in writing after the conference has ended and send the discussions to authors for comments. The completed discussions will be published with the papers if possible, or in the June and December Discussion Sections.

Constructive discussions in CORROSION technical material may be submitted at any time for publication.

Oil Ash Corrosion, Refractory Applications Are Among Topics

One of the nine papers in the Elevated Temperature Corrosion Symposium pertains to refractories, their corrosion resistant properties and application and potentialities of special refractories.

Two other papers deal with the oil ash corrosion problem. The remaining papers discuss high temperature corrosion in the reduction of metals, zirconium in hydrochloric acid, effect of silicon on high temperature oxidation, iron and nickel base supper alloys, coatings for protection against high energy fuel products and corrosion resistance of high nickel content steels to high temperature lead.

ABSTRACTS

Effect of Silicon on High Temperature Oxidation by John F. Radavich, Purdue University, West Lafayette, Ind.

Growth of oxide films at 600 and 800 C on a series of stainless steels with silicon contents from 0.17 to 3.55 percent was studied by electron microscopy, electron diffraction, X-ray diffraction and X-ray fluorescence analysis. Oxide scales and sub-scales formed at 1000 C were studied optically in cross section, by X-ray diffraction and by fluorescence analysis.

Results show that as the silicon content is increased the oxidation resistance increases rapidly. At the high silicon level (3.55 percent) a thin oxide film is formed at 600 and 800 G and very little oxide scale at 1000 C.

The mechanism of oxidation resistance imparted by the silicon appears to decrease the number of defects in the initial oxide films at the metal-oxide interface. With a smaller number of defects in the film, an enrichment of Cr at the metal-oxide interface and in the thin oxide films occurs, and the diffusion rate of iron outward to form the oxide scale is retarded greatly.

Some results of the effect of silicon on the oxidation of a commercial alloy containing Mo are discussed.

Corrosion of Zirconium in Hydrochloric Acid at High Temperatures and Pressures by W. E. Kuhn, Carborundum Co., Niagara Falls, N. Y.

Corrosion of zirconium was studied in the temperature range of 100 to 250 C in aqueous solutions containing 5 to 37 percent by weight of hydrochloric acid. Results of studies showing dep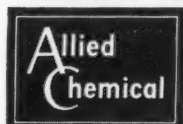endence of corrosion rate on temperature and time are discussed in terms of reaction kinetics. Experiments were conducted to show the dependence of corrosion on the metallurgical structure of zirconium. Corrosion reaction was found to be sensitive to hydrogen adsorbed in the zirconium lattice during the course of the reaction.

High Temperature Corrosion Problems in the Reduction of Some Metals From Their Ores by R. J. Law, Inco of Canada Limited, Toronto, Ont.

Uses and behavior will be discussed of some metallic materials of construction in various steps in the reduction of a number of nonferrous metals. Reduction systems considered are roasting, smelting and refining processes employing elevated temperatures.

Corrosion of Type 310 Stainless Steel by Synthetic Oil Ash by Hugh L. Logan, National Bureau of Standards, Washington, D. C.

The minimum temperature at which a mixture of V_2O_5 and Na_2SO_4 or $NaVO_3$ attacked Type 310 stainless steel was 1075 F (67% V_2O_5 + 33% $NaVO_3$). On the first heating V_2O_5 + $NaVO_3$ reacts to produce O_2 which was consumed on prolonged heating in a closed system.

A second phase is produced at the interface between steel and a vanadium compound heated in the 1075 to 1650 F range. There is some evidence that this phase penetrates into the steel at the grain boundaries. Specimens of steel heated in contact with a vanadium compound above 1650 F contain nodules of a second phase at the grain boundaries.

Spectrochemical analyses of the steel and slag (formed by heating the oil ash mixture) indicated that some vanadium had penetrated the steel and that the slag contained components of the steel in the same proportions as they were present in the basis metal.

Corrosion-Resistant Special Refractories—Their Applications and Potentialities by Roy W. Brown and H. G. Noble, Carborundum Co., Perth Amboy, N. J.

Although metals are generally used to combat corrosion, more severe corrosion conditions often coupled with abrasion, erosion and moderate to high temperatures create a demand for other materials having properties that make them suitable substitutes for metals. Characteristics of special refractories with present day uses are discussed. Their metal-like properties of thermal conductivity, hot compressive strength and abrasion resistance are given plus a description of how products can resist extreme conditions of tension, thermal shock and impact by redesign.

Corrosion Resistance of High Nickel Content Steels to High Temperature Lead by William Lechnick, Westinghouse Electric Corp., Pittsburgh, Pa.

Corrosion resistance of nickel-bearing steels to lead at 1400 to 1500 F was enhanced when nickel and zirconium were added to the lead. Materials were tested under static conditions for 340 to 5252 hours.

Test procedures and methods used to purify lead are described. Data on corrosion rates with and without inhibitors are presented. Results of microscopic examination of test specimens are included.

Coatings for Protection Against High Energy Fuel Combustion Products by W. M. Spurgeon, General Electric Co., Cincinnati, and David Roller, Wright Patterson AFB, Ohio.

Combustion in aircraft gas turbines of boron containing high energy fuels produces deposits containing boric oxide, boron and carbon. Engine parts in contact with these deposits can be corroded severely. Protective coatings are needed for some of these parts. Requirements which must be met by these coatings are outlined. Materials suitable for coating purposes and methods of application are discussed.

Iron and Nickel Base Super Alloys With Improved Elevated Temperature Properties by Norman R. Harpster, Universal-Cyclops Steel Corp., Bridgeville, Pa.

Vacuum melting methods currently employed commercially for super alloys are briefly described. The effects of vacuum melting and certain modifications in the chemistry on the high temperature properties of iron and nickel base alloys are discussed. Use of higher titanium and aluminum contents and controlled additions of minor amounts of boron and zirconium are the most important chemical modifications. A brief description of the effects of these additions on creep rupture properties is also given. The tensile properties, rupture strength and oxidation characteristics of iron and nickel base super alloys which have recently become of commercial interest are compared with established high temperature materials.

Present Status of the Oil Ash Corrosion Problem by C. J. Slunder, Battelle Memorial Institute, Columbus, Ohio.

January,

General Corrosion

High Purity Water

Problems With Boron-Containing Fuels, Beverage Cans on Agenda

An evaluation of construction materials to handle boron-containing high energy fuels is one subject included in the General Corrosion Smyposium. The unique corrosion and compatibility problems presented by the new high energy fuels are discussed.

Three other subjects in this symposium pertain to corrosion processes in carbonated beverage cans, evaluation and improvement of methods for detecting intergranular corrosion susceptibility in aluminum alloys and corrosion of metals by chromic acid solutions.

ABSTRACTS

Corrosion Processes in Carbonated Beverage Cans by E. L. Koehler, J. J. Daly, Jr., H. T. Francis and H. T. Johnson, Continental Can Co., Chicago.

This work was undertaken to minimize the occurrence of perforations and excessive iron pick-up in carbonated beverage cans. The corrosion mechanism was found to be one of attack on the steel base stimulated by reduction processes occurring at areas of exposed tin or other cathodic regions. The best solution to the problem was found to be in limiting the galvanic current in the can by reducing the corrosivity of the beverage and control of metal exposure in the can.

Short-time test methods were devised to evaluate the corrosivity of beverages. A low air content was found to be essential and control over other depolarizers in the beverage led to lower corrosivities. Improvements made in the organic coating systems and metal exposure in the side seam and double seam regions reduced corrosion currents so that perforations were no longer a problem and so that iron pick-up was effectively reduced.

Evaluation of Materials of Construction for Boron High Energy Fuel Production by William R. Gibson, Callery Chemical Co., Callery, Pa.

Because they involve an unexplored area of chemistry, the boron-containing high energy fuels and intermediates present unusual and sometimes unique corrosion and compatibility problems. The major concern has been finding elastomers, gasket materials and greases compatible with these materials. Stainless steel has been the primary construction metal for bench scale and pilot plant operations. A study of the corrosion rates of other metals using the electrical resistance method is now in progress.

Corrosion of Metals by Chromic Acid Solutions by John W. McGrew and Ted M. Swain, Solvay Process Division, Allied Chemical Corp., Baltimore.

Data are presented relative to the corrosive effect of chromic acid on a group of ferrous and non-ferrous materials. In a quiescent system, chromic acid concentrations of 5 to 50 percent at both room temperature and 180 F were investigated. Exposure time was 2 to 3 days.

Based on a 20 mpy corrosion rate, a wide range of metals can be considered for room temperature applications with the chromic acid concentrations studied. Selection at elevated temperatures is more critical because most of the metals tested did not meet the 20 mpy criteria in chromic acid solutions greater than 10 percent.

Critical Evaluation and Improvement of Methods for Detecting Intergranular Corrosion Susceptibility in Aluminum Alloys by Sara J. Ketcham and Walter Beck, Aeronautical Materials Laboratory, Naval Air Material Center, Philadelphia.

The NaCl-peroxide and electrolytic methods and modifications were studied in this paper. Interesting results were obtained when NaBr was substituted for NaCl in the NaCl-peroxide test.

Results with the electrolytic method show good correlation with results of the NaCl-peroxide test, but the latter is more sensitive for Al-Cu alloys. Effect of quenching rates on electrochemical behavior of allows is given by corrosion current and potential diagrams. Electrochemical processes by which various methods accelerate intergranular corrosion are discussed.

Radioactivity From Corrosion In Reactors to Be Considered

Radioactivity from corrosion and wear in pressurized water reactors is the subject of one paper in the High Purity Water Symposium. Other papers deal with corrosion of aluminum-nickel alloys in high temperature aqueous service, stress corrosion of Type 410 stainless steel and corrosion of metallic materials in pile irradiated water.

ABSTRACTS

Radioactivity From Corrosion and Wear in Pressurized Water Reactors by W. T. Lindsay, Jr., and B. G. Schultz, Westinghouse Electric Corp., Pittsburgh.

Structural integrity and proper mechanical functioning are necessary but not sufficient conditions for satisfactory application of materials in pressurized water reactor plants. Another important consideration is the effect on plant radioactive contamination. Constant vigilance is necessary to maintain the relative ease of accessibility for direct maintenance which is one of the major advantages of this type of power reactor. Several examples are cited of the effect of material selection, design and control of coolant composition on radioactivity problems.

Corrosion of Aluminum-Nickel Alloys in High Temperature Aqueous Service by G. J. Biefer and F. H. Krenz, Atomic Energy of Canada, Ltd., Chalk River, Ont.

The effect of minor additions of Zr, Be and Ti upon the corrosion resistance of Al-Ni-Fe-Si alloys in high purity water has been investigated. The most benefit was obtained by the addition of Be and Ti with or without Zr. The best alloy had the composition 2 percent Ni, 0.5 percent Fe, 0.2 percent Si, 0.2 percent Ti, 0.05 percent Be and 0.05 percent Zr with the balance Al. Its corrosion rate in static water at 300 C was 0.5×10^{-3} inches per year.

Dynamic tests in water at 260 C at a linear velocity of 20 feet per second have shown that the erosion reported previously could be almost eliminated by placing a saturator with a large area of aluminum-nickel in the main circuit of the loop upstream from the corrosion test specimens. This apparently acted by saturating the loop water with dissolved corrosion product. When this technique was used, the dynamic corrosion rate was reduced from the previous rate $> 45 \times 10^{-3}$ inches per year to about 8×10^{-3} inches per year. Preliminary results indicate that even lower corrosion rates can be obtained by prefilming the specimens in high temperature static water.

Corrosion of Metallic Materials in High Temperature Pile-Irradiated Water by George E.

Galonian, Knolls Atomic Power Laboratory, Schenectady, N. Y.

Irradiation corrosion tests of several metals were conducted in 500 to 600 F water subjected to pile radiation for periods to six months. Weight change results are given for coupon samples exposed in in-pile and out-of-pile portion of dynamic test loops which recirculated high pressure water at velocities to 30 fps. Two water conditions were investigated: dionized neutral water and pH 9 ammoniated water cycled to produce short-time conditions of low pH and high oxygen content.
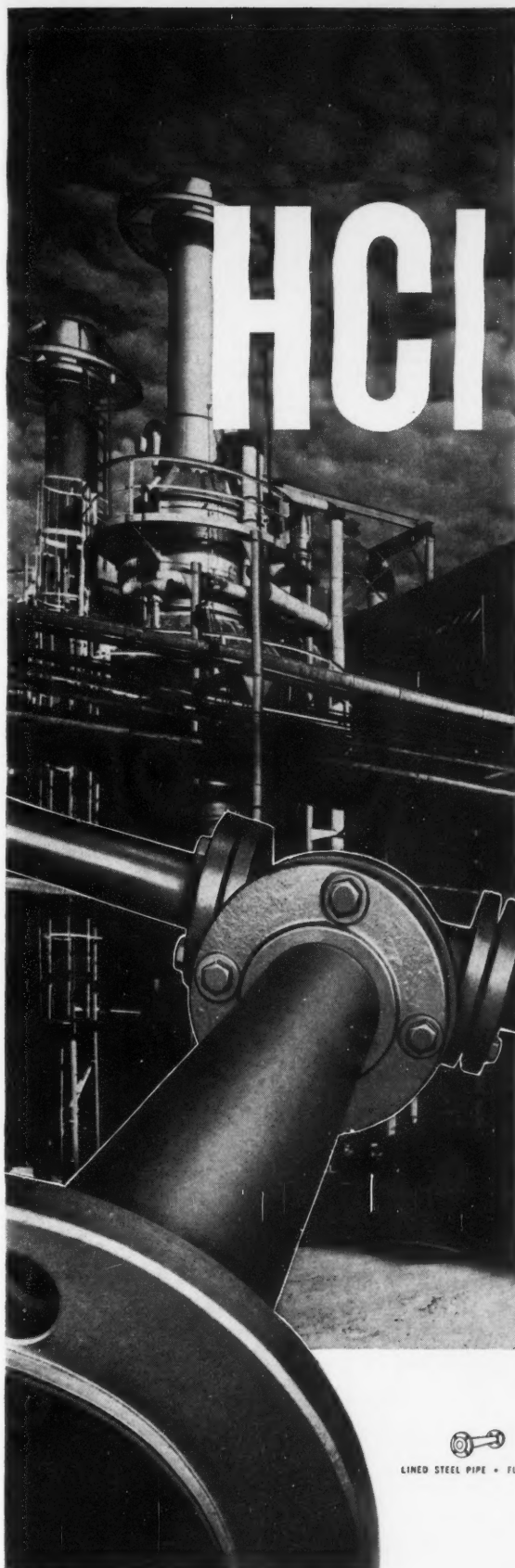
The amount of loose corrosion deposit picked up by the various materials is given and also the amount of adherent scale retained and estimated scale loss by some of the metals. Each material was examined microscopically and metallographically after tests.

Measurements were made of the contamination level of materials exposed out-of-pile and decreases effected by scale removal.

Marine Corrosion

4 Papers
Fri., March 20
2-5 pm

4 Papers
Tues., March 17
9-12 am

Oil and Gas Production

Rubber and Plastics Versus Marine Environment Are Topics

Use of rubber and plastics for corrosion control of shipboard equipment is the subject of one of the four papers in the Marine Symposium. Means of protecting pipe lines, valves and miscellaneous marine equipment subjected to corrosion from sea water and electrolytic action by rubber and plastics are described.

Other papers in this symposium pertain to new instruments and techniques for accurate measurement of corrosion rates, anodes for impressed current in sea water service and developments in controlling cargo tank corrosion.

ABSTRACTS

Developments in Controlling Cargo Tank Corrosion by J. Franklin Koehler, Esso Shipping Company, New York City.
The corrosion wastage typical to clean and dirty service tankers is described, and the magnitude of structural repair costs resulting from this corrosion are illustrated. A summary is given of the effectiveness and cost of both cathodic protection and chemical inhibitor corrosion control systems used on several clean-service vessels.

Coating application costs and operating experience of vessels with coated compartments are reviewed. The relative advantages and disadvantages of using coatings, cathodic protection, chemical inhibitors or combinations thereof for controlling corrosion on new vessels are investigated.

Anodes With Impressed Current in Sea Water Service by T. P. May, The International Nickel Co., Inc., Harbor Island Testing Station, North Carolina.
Results of sea water tests on anode materials are given in detail. These tests include low velocity, high velocity and sea water as well as silt and sand in the sea water location. Data are recorded for steel, silicon iron, graphite, lead alloys, platinum and other noble metals. All the materials in this group have not been investigated under all of the conditions mentioned.

New Instruments and Techniques for Accurate Determination of Corrosion Rates in the Marine Industry by Dwight J. Evans, Engineering Test Services, Inc., Tulsa.
Developments, improvements in techniques, instruments and accessories used to provide accurate corrosion rate data are discussed.

The system of cross-checking resonant frequency data and calculating thickness within one percent accuracy is described. Present adaption of the new cathode ray tube direct reading instruments and the latest techniques for efficient use are discussed with a comparison of the various instruments.

Controlling Marine Corrosion With Rubber and Plastics by J. A. Thompsen, American Hard Rubber Company, New York City.
Use of rubber and plastics are described for controlling corrosion of shipboard pipe lines, valves and miscellaneous marine equipment subjected to corrosion from sea water and electrolytic action. Described in detail are the use of various plastics, technical properties, sizes of pipe, fittings and valves, flow characteristics, creep problems and design of pipe lines.

The use of synthetic rubber is recommended for combatting corrosion where the use of conventional materials is not practical or too costly. Various types of synthetic rubbers are described with the methods of application for both the brush-on types of compounds and the vulcanized sheet types of linings and coverings. Advantages and disadvantages of both applications methods are discussed in detail.

Inhibitor Film Test Described In Four-Paper Symposium

Four papers are included in the Oil and Gas Production Symposium. They discuss a simple screening test for the determination of inhibitor film persistence, stress corrosion cracking of tubular goods in the field and selection of equipment and control of corrosion in the production of gas containing high percentages of hydrogen sulfide and carbon dioxide.

ABSTRACTS

A Simple Screening Test for the Determination of Inhibitor Film Persistence by John A. Knox and Roy Stout, Halliburton Oil Well Cementing Co., Duncan, Okla.
A simple screening test similar to the copper ion displacement test has been devised to screen corrosion inhibitors to be used in the inhibitor squeeze process. Unlike most conventional corrosion tests designed to determine the relative effectiveness of inhibitors at low concentrations, this extended copper ion test screening procedure evaluates the durability of protective inhibitor films formed by relatively high inhibitor concentrations which are used in the squeeze process.

The effect of inhibitor concentrations, adsorption time, adsorption temperature adsorption from various solvents, coupon surface preparation, etc., was studied on the film presistance of a series of chemical compounds thought to have inhibiting properties. This evaluations is based on the length of time required for copper to form the coupon. A comparison was made between

this test and a similar test using hydrogen sulfide as the corrodant.

Selection of Equipment and Control of Corrosion in the Production of Gas Containing High Percentages of Hydrogen Sulfide and Carbon Dioxide by D. R. Finchers, Tidewater Oil Co., Houston.

Stress Corrosion Cracking of Oil Country Tubular Goods by R. L. McGlasson and W. D. Greathouse, Continental Oil Co., Ponca City, Okla.
A brief review of the general problem of stress corrosion cracking is given with the related problem of hydrogen embrittlement. A list is given of the material-environment combinations which have been reported to result in cracking.

Sulfide corrosion cracking and sweet corrosion cracking are considered with a review of the literature on these subjects. A new test method is explained which uses a notched ring of the material loaded to different percentages of the yield deformation. This test gives failures at macroscale deformations well below the yield point without pre-stressing the specimen above yielding. It also gives good time-to-failure reproducibility at sub-yield deformations.

Hardness, applied stress and time-to-failure data are given from tests conducted by the new method. Data indicate that sweet cracking failures are probably sulfide cracking at low H_2S concentrations. Data also demonstrate that time-to-failure is an inverse function of the H_2S concentration and that this rate is probably a function of CO_2 content.

Copies of Papers

Copies of papers presented at the 15th Annual NACE Conference at Chicago can be obtained by registrants only. A procedure has been arranged whereby

1. Persons who register at the conference may order copies of the papers in which they are interested.

2. Orders must be placed at the conference registration desk during the conference.

3. A small charge, sufficient to reimburse NACE for the cost of preparing photographic copies will be made for each paper ordered.

4. Papers ordered will be copied after the conference is over and mailed.

T. J. Hull, NACE executive secretary said the association will not accept orders for copies from persons who are not registered at the conference.

Pipe Line General

4 Papers

Thurs., March 19

2-5 pm

7 Papers

Session One

Thurs., March 19

9-12 am

Session Two

Thurs., March 19

2-5 pm

Plastics

Protection of Offshore Pipe One of Topics Discussed

Details of a cathodic protection system for a 22-inch offshore steel pipe with several novel features is one subject in the Pipe Line General Symposium. Features of this system were cathodic protection applied continuously during installation and built-in testing facilities along the pipe line.

Other subjects in this symposium deal with the use of magnesium for cathodic protection of pipe lines in high resistivity soil, accelerated protection in an emergency situation and equivalent electrical circuit analogy of structure to soil potentials.

ABSTRACTS

Equivalent Electrical Circuit Analogy of Structure to Soil Potentials by Roy O. Dean, Pacific Gas & Electric Co., Emeryville, Cal.

When cathodic protection measurements are being analyzed, equivalent electrical circuit analogy is helpful in understanding structure to soil potentials. Made with extreme care and precision, these measurements sometimes appear erratic and anomalous. The equivalent circuit explains (1) why reference electrode location usually is not important when testing well coated structures, (2) why extremely high potentials measured near cathodic stations are false, (3) why abnormally low and false potentials are measured on bare or poorly coated structures which are adequately protected and (4) why structure to soil potentials cannot be used as a criterion of cathodic interference except with proper consideration of all associated factors.

Methods are discussed of other useful ways for using soil potential measurements. Conclusions indicate that in measuring structure to soil potentials the reference electrode must be at the defined remote position to obtain authentic results.

Blitzkrieg Cathodic Protection of a High Pressure Products Pipeline by D. N. Miller, Southern Pacific Pipe Lines, Los Angeles.

Various problems encountered and the methods and shortcuts employed to achieve cathodic protection of a pipeline across Central California and Nevada are discussed. The terrain varies from sea-water marshes to High Sierra granite. When the coating was found to be in poor condition with corrosion already begun after only a few months of service, cathodic protection work was accelerated for protection before winter floods.

Use of Magnesium for Cathodic Protection of Pipelines in High Resistivity Soil by A. W.

Peabody, Ebasco Services, Inc., New York City.

A cathodic protection installation is described in which satisfactory protective potentials were attained at about 400 miles of enamel coated pipeline with a total current between 2 and 3 amperes from nine magnesium anode beds. Over-all current consumption was less than 0.5 microamp per square foot. Average soil resistivity at pipeline depth was 120,000 ohm-cm although it dropped to less than 2000 ohm-cm at potential hot-spots. Indicated average coating resistance for the system was about 700,000 ohms per average square foot. Four of the nine anode installations were in soil having resistivity above 10,000 ohm-cm.

Methods are described in which long slender magnesium anodes were used to obtain the necessary current output. Testing facilities and zinc anode electrolytic cells for protection against lightning or electric power surges are also described.

Corrosion Protection Features of the Hyperion Ocean Outfall by Harry J. Keeling, Consulting Engineer, Los Angeles.

Details are presented of the cathodic protection system used on a 22-inch steel pipe extending offshore about 7 miles into 300-ft water at Los Angeles. Multiple layers of coal-tar protective coating were used with a rectifier impressed-current cathodic protection installation. The interior was protected by ½-inch centrifugally spun cement-mortar lining.

Because the pipe was to be in deep water, several novel features were developed: (1) Cathodic protection was applied continuously during installation. (2) The line was designed with built-in testing facilities: a submarine test cable attached at intervals for continuous measurement of pipe potentials during and after installation. (3) Protective coating effectiveness was monitored continuously during installation by electrical recording instruments.

Coating quality was much higher than anticipated. After one year, coating resistance is about 400 kilohms per square foot. Cathodic protection of the pipe line is achieved with a total current less than 0.2 amperes.

Epoxy and Furane Structural Plastics Uses Are Surveyed

A survey of the industrial uses of plastics for corrosion control is given by the seven papers scheduled for the Plastics Symposium.

Glass reinforced plastics, reinforced epoxy and reinforced furane resin applications are discussed in three papers. Other papers deal with chlorinated polyether, plastisols and non-metallic pipe for corrosion control purposes.

A round table discussion will be held after each of the two session for this symposium.

ABSTRACTS

Polyester Fiber Glass Equipment: Case Histories of Their Use in the Chemical, Petroleum and Allied Industries by Robert E. Barnett and Thomas F. Anderson, Haveg Industries, Inc., Wilmington, Delaware.

Four classes of polyesters with different chemical properties are discussed. Service conditions are discussed of tanks, towers, covers, hoods, ducts, fans, stacks and fume scrubbers made of

polyester fiber glass. Length of service ranges from 2 to 8 years.

Polyester fiber glass lined steel ductwork and steel and concrete tanks are illustrated, and discussion is given to conditions requiring the use of linings.

A table with over 5000 service recommendations is discussed. Recommended procedures for material selection are also given.

Plastisols for Corrosion Control by J. Watson Pedlow, Quelcor, Inc., Chester, Pa.

Recent applications and developments are dis-

cussed in the plastisol field both in America and abroad. Protective coatings, resulting from new formula modifications, which show unusual resistances to chemicals and high temperatures are reviewed with laboratory evaluations and case histories of actual field exposures.

Non-Metallic Pipe for Liquid Corrosives by C. A. Burt, American Hard Rubber Co., Chicago.

Metallics and non-metallics are compared, showing the number of different corrosive solutions handled by each. The proper selection of non-metallics is discussed.

Reinforced Furane Resin Equipment for the Chemical Industry by John Delmonte, Furane Plastics, Inc., Los Angeles.

Primary emphasis is on the structural laminates prepared from furane resins, comparing the room temperature curing system involving field applications and those systems prepared under heat and slight pressure. Data presented shows the chemical resistance of different cured laminates prepared from these resins. Chemical resistance tests show not only the loss of strenght upon immersion in warm water and the warious acids and alkalies but also the strength-retention properties after immersion under stressed conditions.

Combatting Corrosion With Penton—Chlorinated Polyether by C. S. Miller and J. B. Martin, Hercules Powder Co., Wilmington, Delaware.

Physical properties, chemical resistance and field application data are given on the new chlorinated

Protective Coatings

6 Papers

Session One

Mon., March 16

2-5 pm

Session Two

Tues., March 17

9-12 am

8 Papers

Session One

Mon., March 16

9-12 am

Session Two

Mon., March 16

2-5 pm

Symposium to Consider Tests, Applications and Case Histories

Divided into two sessions of five papers each, each session of the Protective Coatings Symposia will be followed by a panel discussion.

A diversity of information pertaining to protective coatings is covered by the papers: laboratory and field tests of coatings, a 30-year history of tank car interior coatings and oil refinery applications of thick film synthetic coatings.

One paper discusses protective coating engineering.

A B S T R A C T S

Oil Refinery Applications of Thick-Film Synthentic Coatings by R. W. Maier, W. B. Cook and R. B. MacQueen, Gulf Oil Corp.
Coatings discussed include hot spray vinyl, catalyst cured epoxy, catalyst cured phenolic, catalyst cured epoxy-modified phenolic and high-film-build alkyd coatings. Advantages derived from their application to surfaces of oil refinery equipment are given. Field experiences with applications of these coatings on various equipment surfaces exposed to a wide range of contact media and conditions are also described.

Field Experience With Corrosion Resistant Coatings by Newell D. Casdorph, Union Carbide Chemicals Co., Port Lavaca, Texas.
Generic types of materials used, performance of materials, simplified painting program records and an analysis of program costs are presented. Training of staff members for the coatings department is also discussed. Hazards involved in spray painting and sandblasting are given with an investigation of damage caused by sandblasting and the necessary protection for mechanical equipment.

From the Panel to the Plant by D. A. Ballard and V. B. Volkening, Dow Chemical Co., Freeport, Texas.
A point testing program is related to the size of the paint maintenance cost and management's desire to reduce this cost. Procedures are described for a paint panel testing program. Particular attention is given to the experimental design, evaluation of panels, and calculation and interpretation of the data. Observation of pitting of the steel is used as an important analytical tool. Large scale controlled field tests follow the panel testing. Materials and methods evolving from these tests become accepted standards.

A Laboratory Paint Test Program by R. E. Gackenbach, American Cyanamid Co., New York City.
A laboratory paint test program is described as a method of screening paints to select the specific item that will give the exact degree of protection needed for specific applications. The benefits and pitfalls of such a program are outlined. The paints that fail in the laboratory will probably fail in the field. Those that show promise in the lab must be field tested to determine final suitability.

Plastic Symposium—

polyether, Penton. Comparative dimensional stability under relatively high operating temperature conditions with other plastics is discussed. The use of polymer is presented in such widely diversified products as valves, bearings, precision gears, high tensile strength rope and packaging films under severe corrosion conditions.

Handling of Corrosive Fumes Using Glass Reinforced Plastics by R. B. King, Heil Process Equipment Corp., Cleveland.
A general description of polyester, epoxy and furane resins is given with their physical and chemical properties. Limitations, use of fiber glass and asbestos and synthetic fiber reinforcement are also discussed.

Precaution to be observed in immersion service and the use of field applied reinforced plastics are given.

Epoxy Resin Structures in Corrosion Resistant Applications by Elliott N. Dorman and William Ibsen, Ciba Products Corp., Kimberton, Pa.
This paper details the relative chemical resistance, physical properties and engineering design requirements in the application of various combinations of epoxy resins with natural and synthetic reinforcing materials. Field applications are discussed of equipment for chemical, petroleum and allied industries.

Pulp & Paper Industry

Digester Corrosion and New Bonding Process to Be Covered

The eight papers scheduled for the Pulp and Paper Symposium cover the corrosion control problems peculiar to this industry, ranging from paint maintenance programs, digester corrosion and plastic applications to a study of the electrochemical mechanism.

Other papers present the role of the corrosion engineer in this industry, use of a new versatile bonding process and recent investigations of corrosion in the southeastern states.

A B S T R A C T S

Hortonclad by R. A. Davis, Chicago Bridge & Iron Co., Birmingham.
A new versatile bonding process for producing clad plates is described. Employing high vacuum, heat and atmospheric pressure, the Hortonclad process is not limited to the usual metals used in clad plates nor even in the backing plate material itself.

A brief history of the process is given, the process of manufacture is described and fabrication methods are discussed. Available sizes and thicknesses, quality control, inspection and tests and special applications such as channeled Hortonclad are given. Cladding alloys now available commercially in Hortonclad plates are listed with backing plate materials. Several additional alloys or metals now in development are discussed separately.

Neoteric Answers to Corrosion Problems in the Pulp and Paper Industry in the Southeast by

Arthur B. Smith, Amercoat Corp., Jacksonville, Fla.
This paper presents results of a ten-year field investigation into the problems of protecting steel and concrete structures in the pulp and paper industry of the southeastern USA. Methods of surface preparation, application techniques and selection of proper coatings for the most satisfactory and economical protection are discussed.

Consideration is given to the most troublesome areas and the conditions under which application must be made to maintain protective coating systems while plants are in operation and under construction.

Actual field service data are given with a comparison of of over-all costs by using modern coating methods as opposed to conventional methods.

The Corrosion Engineer's Role in the Pulp and Industry by Roy P. Whitney, The Institute of Paper Chemistry, Appleton, Wisconsin.
New processes and technology emphasizing more

efficient use of raw materials, greater speeds, higher temperatures and pressures have presented more severe corrosive environments in the pulp and paper industry and have focused attention on the need for better undestanding of corrosion and its control in the industry.

Two important trends within the industry are discussed: increased volume of corrosion research and recognition of the need for competent corrosion engineers and specialists.

Study of the Electrochemical Mechanism Producing the Conversion From the Active to the Passive State by W. A. Mueller, Pulp and Paper Research Institute of Canada, Montreal.
The characteristic electrochemical data on the active state as the Flade potential and on the passive state are summarized. A set of equations is derived which describes the density of the anodic dissolution current as a function of the

Refinery Industry

9 Papers

Session One

Mon., March 16

9-12 am

Session Two

Mon., March 16

2-5 pm

A B S T R A C T S

Corrosion in Cooling Tower, Conversion Systems Considered

A variety of subjects are included in the nine papers for the Refinery Industry Symposium. Corrosion caused by residual welding slag in hydrogen reforming furnace tubes and corrosion in hydrocarbon conversion systems and cooling tower systems are some of the subjects included.

Other papers deal with corrosion resulting from burning methane with oxygen, high temperature sulfide corrosion, chemical cleaning in refineries and petrochemical plants and selection of alloys for processing equipment.

Two papers pertain to the effects of carbon monoxide: one on the deterioration of heat resisting alloys and the other on elevated temperature attack on steels.

Preliminary Investigation: The Deteriorating Effect of Carbon Monoxide Atmospheres on the Heat Resisting Alloys by E. N. Skinner and R. J. Raudebaugh, The International Nickel Co.

A review of this behavior as encountered in practice and results of limited laboratory experiments made in an attempt to reproduce the effect under known conditions are described. Variables in the lab tests include surface finish and the influence of crevices and notches. Inconel, Incoloy and stainless steels are included in the experimental investigation.

Experience With Elevated Temperature Attack on Steels by Hydrogen, Carbon Monoxide Rich Gas Mixture by W. B. Hoyt and Robert M. Caughey, M. W. Kellogg Co., New York City.

Carbon steel and stainless steel equipment exposed to gas mixtures rich in hydrogen and carbon monoxide at temperatures between 800 and 1200 F have been attacked with resulting loss of metal. The conditions under which this attack have been observed in a coal-to-oil synthesis plant, and the nature of the metal deterioration are described. The mechanism of this type attack is not fully understood although a possible gas-metal reaction is postulated.

Selection of Alloys for Processing Equipment by A. J. Freedman, G. F. Tisinai and E. S. Troscinski, Standard Oil Engineering Research Department, Whiting, Indiana.

Alloy selection for any new unit operating under conditions severely corrosive to carbon steel must include careful consideration of the many factors which may influence corrosion resistance. Corrosion rates of many special alloys are affected by metal structure. Variables such as metal shape, size, fabrication procedures, heat treatments and composition should be evaluated carefully. Possible metallographic changes during service life must be considered also. Effects of corrosive environments, both during operation and when off stream, must be tested.

A materials evaluation program should be a continuous development of any new process, beginning at the bench scale pilot plant stage. The materials study should continue after the construction of the unit because actual stream conditions can differ significantly from those used in preliminary tests. Sensitive locations where corrosion might occur should be monitored continuously with corrosion probes, both to provide warning of dangerous conditions before trouble develops and to develop a history of normal corrosion rates for the process.

Chemical Cleaning of Equipment in Refineries and Petrochemical Plants by Lambert N. Klinge and Johan Selman, N. V. de Bataafsche Maatschappij, The Hague, The Netherlands.

This paper is an abstract of a manual containing information and experience collected on the chemical cleaning of equipment at several refineries and petrochemical plants of companies in the Royal Dutch-Shell Group. The manual was designed to serve as a guide for chemical cleaning.

High Temperature Sulfide Corrosion by Gerard P. Canevari and Frank K. D'Ambra, Esso Research and Engineering Co., Linden, N. J.

Pilot plant tests were conducted to determine the corrosion rates of metals to be used for furnace tubes in steam cracking units which reach temperatures of 1700 to 2100 F with feedstocks containing up to 1 wt percent sulfur, conditions suitable for severe corrosion.

Test work on several nickel-chromium-iron alloys and coated alloys is discussed. Results proved to be contrary to expectations.

An Industrial Experience of Severe Metal Wastage Resulting From Burning Methane With Oxygen by F. Eberle and R. D. Wylie, Babcock & Wilcox Co.

Severe metal wastage was experienced on 18-8 Cb (Type 347) and 25Cr20Ni (Type 310) used in the construction of a gas generator in which methane was burned with oxygen to produce carbon monoxide and hydrogen for fuel synthesis of the Fischer-Tropsch type. The mode of attack varied with temperature. At the highest temperatures, above 1650 to 1800 F, it consisted of straight oxidation, progressing intergranularly. With decreasing temperatures, heavy carburization with occasional signs of interspersed oxidation manifested itself. As temperatures declined further, cycling carburization, oxidation and reduction were observable, resulting in severe metal wastage.

Typically attacked metal surfaces consisted of a semi-scale containing tiny globules of metallic particles surrounded by carbon or graphite interspersed with oxide. Tests with specimens of numerous steels and alloys installed at various locations in the reactor showed that the most resistant materials were those which best resisted carburization, that is, nickel, Monel, Inconel, 27 chrome-iron, copper and packcalorized material.

Corrosion and Deposition Control in Cooling Tower Systems by R. P. Gulley, Gulf Oil Corp., Port Arthur, Texas.

Various approaches to controlling deposition and corrosion in cooling tower systems are discussed. These approaches vary in complexity with the availability and quality of make-up water, type of heat transfer equipment served, range of temperatures encountered and required periods of time between equipment cleaning.

Corrosion inhibitors most frequently applied to cooling tower systems are reviewed individually. Relative advantages and disadvantages of such inhibitors as chromates, nitrites, polyphosphates, zinc, fluorides, ferricyanides, reduced chromate and organics are discussed.

Modern treatments generally control deposition by operating at a pH level below that where scale forms. In applications with high severity, agents to broaden solubility limits are needed. These agents are classified and discussed. Included in this discussion are agents to control fouling by biological growths.

Factors which affect the efficiency of treatments are pointed out. Heat transfer equipment designers must consider those factors which influence treating such as metals utilized, water velocities, and temperature levels. Methods of determining treating efficiency are presented.

Corrosion in Hydrocarbon Conversion Systems by F. A. Prange, Phillips Petroleum Co., Bartlesville, Okla.

Under some inexactly defined conditions, steels and alloys are attacked by atmospheres resulting from oxidation of hydrocarbon. In a fixed-bend catalytic system for dehydrogenation of

Pulp and Paper—

metal to electrolyte potential difference and the pH value.

These equations not only permit the calculation of the Pourbaix diagram, the Flade potential and the current density in the passive state but also formulate the partial anodic current density in the range of the conversion from the active to the passive state. The calculation of the decrease of current density with increasing potential is based on the working hypothesis that an increasing fraction of atoms becomes covered by a protective film and is prevented from dissolution, the film-free atoms being dissolved at an undiminished rate.

This hypothesis may not necessarily be accurate, but it lends itself better to the calculation than the assumption of an increasing degree of protection of individual surface atoms. With increased potential the degree of film coverage increases exponentially with a higher exponent than does the current density at the film-free fraction of the surface. Thus in the process of the conversion from the active to the passive state, the current density is reduced exponentially to the constant and very low value of the anodic dissolution current in the passive state.

These principles and formulae, derived with respect to the passivating film of iron oxide on iron, are expected to apply to any electrochemical passivity.

A Look at Plant Maintenance Programs in Regard to Corrosion by S. John Oechsle, Jr., Metalweld, Inc., Phildelphia.

The need is emphasized for cost figures to be given to management to justify annual budgets for preventive maintenance programs. Projected information is also needed to show the necessity for annual expenditures to maintain the lowest cost per service year in maintenance programs.

A Modern Approach to Planning a Maintenance Coating Program by M. W. Belue, Jr., Champion Paper & Fibre Co., Pasadena, Texas.

Details of a plan to solve corrosion problems by a coatings program are given. Various phases of the program are discussed: cost, personnel, time and service life expected. Accomplishements of the program over a four-year period are evaluated.

Plastic Applications in the Pulp and Paper Industry by John H. Lux and James M. Brady, Haveg Industries, Inc., Wilmington, Delaware.

Plastics are being used as substitutes for lead, glass, stainless, wood, acid proof bricks, rubber, transite and concrete in the pulp and paper industry. Advantages obtained by use of plastics are discussed.

Typical equipment and installations are described.

Union Bag-Camp Paper Company Experiences With Digester Corrosion by C. S. Porter, Union Bag-Camp Paper Co., Savannah, Ga.

Data presented were collected from a plant where both semi-chemical and kraft pulp are cooked in vertical stationary digesters by direct steam. A summary is given of the digester inspection procedures used and the system of reporting corrosion data. Collected over a period of 22 years, the data cover about 60 digesters. The corrosion rates of 11 different digester construction materials (including Inconel, stainless steel, welded overlay and carbon brick) and the economic factors involved in their use are compared. The results of sample plate tests of various alloys and coatings are discussed.

Utilities Industry

5 Papers
Thurs., March 19
9-12 am

Corrosion Control Discussed For Nuclear Power Plant

The Utilities Industry Symposium includes five papers dealing with corrosion control problems.

Cathodic protection of underground lead sheath cables is one subject; another paper describes a distributed anode system in an urban area.

Qualification of Inconel for nuclear power plant applications is discussed in another paper.

Auth

ABSTRACTS

Problems of an Electric Utility Involving Corrosion Control Practices by D. E. Simmons, Houston Lighting & Power Co., Houston.

Tests fail to indicate that electric service ground connection to the water piping system causes corrosion of the piping system. The use of sacrificial anodes to protect individual water line services can result in inadequate grounding due to the insulating coupling used. The National Electric Service Code requires installation of supplementary grounds in such cases. Electric service connections to cathodic protection rectifiers requires special precautions. The use of zinc or magnesium anodes for service grounds is recommended for all rectifier installations.

Cathodic Protection of Lead Cable Sheath by Walter H. Bruckner and Ole G. Jansson, University of Illinois, Urbana.

Results of laboratory tests with gradient lead cathodes in environments of high pH level are described. By observation of the corrosion limit and corresponding potential, the cathodic protection requirements were defined for permanence of metallic lead as a function of the environment's pH. The increment of cathodic potential required for interface protection of partially immersed lead cathodes was also defined for laboratory tests cells. The effects of overprotection and of a soil barrier to diffusion are shown to increase the susceptibility of the lead system to corrosion loss during periods of minimum current supply.

The instability of a lead electrode was evident in attempts to measure static potentials except under precisely controlled conditions not obtainable in the field. The authors recommend that potentials in the field be obtained with other standards than the lead electrode.

Qualification of Inconel for Nuclear Power Plant Applications by H. R. Copson, W. E. Berry K. H. Vogel, Yale Solomon, G. R. Pease and W. A. Fragetta.

A Distributed Anode System in an Urban Area by James P. McArdle, Jr., American Telephone and Telegraph Co., Atlanta.

Problems are discussed involved in applying cathodic protection to cables in an underground conduit system in an urban area where resistivity conditions are not uniform and where other subsurface structures are present.

A distributed anode system was employed with anodes located along a pole line at the base of selected poles, one anode at each pole. The anodes were interconnected by a continuous length of insulated wire placed aerially on the pole line.

Impressed current was supplied to the anodes by three small rectifiers with a total output current of 8.3 amperes. Approximately 21 sheath miles of cable are protected; 16 are of bare lead sheath.

Current picked up by other structures is small and can be drained satisfactorily by resistance bonds with little increase in electrical power requirements for equalizing potentials to these structures.

Duct Anode Development and Experience in the Protection of Underground Cables From Corrosion by J. E. Johnson, Philadelphia Electric Co., Philadelphia.

Operating experience has shown that the life of graphite anodes is very short when used underground in silt filled ducts. Gases liberated by the electrolysis process and trapped by silt attack the graphite binder, tape adhesive and many wire insulations.

Tests indicate a long life for high silicon iron anodes in ducts containing silt. Black, high molecular weight polythylene appears to be resistant to the attack experienced on other anode wire insulations.

Several improvements in the assembly of the anode elements have also resulted in substantial savings such as elements assembled on a continuous wire to eliminate mechanical connectors and splices, better electrical and mechanical connection between the header wire and element and improved sealing of the header wire into the anode.

Increasing the spacing of the elements in the anode reduces costs. The optimum element spacing can be determined by test.

Refinery Symposium—

butane, the metal loss which contaminates the catalyst with a fine oxide dust causes undesirable side effects. The way in which the metal loss occurs is described, and the effects of alloying agents on both laboratory tests and actual equipment are mentioned. Some examples of metal dusting give a clue to the mechanism of metal loss but are not complete enough to define fully.

Corrosion of Hydrogen Reforming Furnace Tubes by Residual Welding Slag by Kenneth L. Moore, Tidewater Oil Co., Delaware.

Rapid corrosion of hydrogen reforming furnace tubes was experienced during high temperature operation. The attack was initiated by residual welding slag and was accelerated by the presence of sulfur and reducing conditions. Thorough sandblasting is essential for complete removal of the welding slag and elimination of its associated corrosion problem.

Authors of Technical Papers 15th Annual NACE Conference

Anderson	Aschan	Ballard	Barnett	Beck	Belue
Berry	Biefer	Bruckner	Brown	Burt	Canevari
Casdorph	Caughey	Clary	Condry	Cook	Copson
Craig	Daly	D'Ambra	Davis	Dean	Delmonte
Dorman	Eberle	Evans	Fincher	Fragetta	Francis

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Au

Gackenbach   Galonian   Gegner   Gibson   Gilman   Greathouse

Gulley   Harpster   Herman   Hoyt   Husock   Ibsen   D.

H. T. Johnson   J. E. Johnson   Wayne Johnson   Keeling   Ketcham   Knox

J. F. Koehler   Krenz   Kuhn   LaQue   Law   Lechnick   Ra

Lewis   Logan   Long   MacQueen   Maier   Marsh   Sp

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May	McArdle	McDowell	McGlasson	McGrew	Merrick
D. N. Miller	Mueller	Noble	Oechsle	Peabody	Pease
Pedlow	Piccardo	Pines	Porter	Prange	Priest
Radavich	Roller	Simmons	Skinner	Smith	Solomon
Spivack	Spurgeon	Stout	Swain	Thompsen	Tisinai

Authors of Technical Papers 15th Annual NACE Conference

Troscinski   Uhlig   Vogel   Volkening   Wellington   Whitney

Wilson   Young

15th Annual Conference
BIOGRAPHIES

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WARREN E. BERRY is project leader, Corrosion Research Division, Battelle Memorial Institute, Columbus, Ohio. His work includes high temperature and high pressure corrosion reactions, fuel-element corrosion and materials for reactor construction. He is a graduate of Ohio University.

G. J. BIEFER is affiliated with the Corrosion Group of the Research Metallurgy Branch, Atomic Energy of Canada Limited at Chalk River, Ontario. Formerly he was with E. I. du Pont de Nemours in Virginia. He has a BS and PhD in physical chemistry from McGill University.

R. W. BROWN is manager of Technical Sales of the Refractories Division, Carborundum Co., Perth Amboy, N. J. A graduate ceramic engineer, he has been a field engineer and has written several papers on the use of nonmetallics.

WALTER H. BRUCKNER is a research associate professor of electrical and metallurgical engineering at the University of Illinois and is technical director of the Cathodic Protection Laboratory there. Prior to his association with the University in 1938, he was on the research staffs of the Naval Research Laboratory, American Smelting and Refining Company and Crucible Steel Co. He has publications in physical metallurgy, fatigue of metals, welding, brittle fracture of steel and corrosion. He is a member of AIME, ASM, AWS, and NACE.

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ROBERT H. CAUGHEY is chief metallurgist with the M. W. Kellogg Company, New York City, Formerly he was associated with the U. S. Steel Corp., and A. O. Smith Corp. He has a BS in metallurgical engineering from Pennsylvania State University.

W. B. CLARY is engaged in cathodic protection and corrosion engineering with the Esso Research and Engineering Company. Before joining Esso in 1937, he was employed by Henry Souther Engineering Co., Hartford, Conn., and Worthington Pump and Machinery Co., Harrison, N. J. He received a BS in mechanical engineering from Rensselaer Polytechnic Institute, where he was also an instructor in mechanical engineering.

JAMES T. CONDRY is manager of Southeastern Division, Corrosion Rectifying Co., New Orleans, La. A graduate of Finlay Engineering College, he formerly was with Service Pipe Line Company. He is a member of NACE.

HARRY R. COPSON is head of the Corrosion Section, Research Laboratory, International Nickel Co., Inc., Bayonne, N. J. Active on many corrosion committees and author of several papers, he has a BS from the University of Massachusetts and a PhD in physical chemistry from Yale.

W. B. COOK is affiliated with Gulf Oil Corporation's Port Arthur refinery in coatings work. He is a graduate of Texas A & M College and is a member of NACE.

W. G. CRAIG is manager of Chemical Products Department at Lubrizol, Wickliffe, Ohio. He has a BS from Pomona University and is a member of NACE, ASTM, ASC and Association of Asphalt Paving Technologists.

JOHN J. DALY, JR., is chief of the Corrosion Research Section, Metal Division, Research and Development Department, Continental Can Co., Chicago. He has a BS in metallurgical engineering from the University of Illinois.

FRANK K. D'AMBRA is associated with the Corrosion Research Group at Esso Research and Engineering Co., Linden, N. J. He has a BS in mechanical engineering from the University of Rhode Island and is a member of ASME.

R. A. DAVIS is staff engineer for Chicago Bridge and Iron Co., Birmingham. Formerly he was with Reeves Brother Company, Alliance, Ohio. He is a member of NACE, AWS and Technical Association of the Pulp and Paper Industry.

ROY O. DEAN is supervisor of the Corrosion Engineering Department in the Bureau of Tests and Inspection, Pacific Gas and Electric Co., Emeryville, Cal. He received a BS in electrical engineering from Tri-State College and is registered in California as a profesional engineer. He has been a member of NACE since its formation.

JOHN DELMONTE is president and general manager of Furane Plastics, Inc., Los Angeles. He has published three books on plastics and adhesives and was technical director of plastics at the I. T. Institute for ten years.

ELLIOTT N. DORMAN is sales manager of the Structural Resins Department at Ciba Products Corp., Kimberton, Pa. Author of several papers on epoxy resins, he has a BS in chemical engineering from Columbia University.

F. EBERLE is chief metallurgical engineer at the research center of Babcock & Wilcox Co. Formerly he was associated with the metallurgical staffs of Cadillac Motor Co., Leeds & Northrup Co., and Carnegie Illinois Steel Corp. He has a PhD in chemical and metallurgical engineering from the Technical University of Munich.

DWIGHT J. EVANS established Engineering Test Services, Inc., Tulsa, Okla., which specializes in ultrasonic thickness measurement for corrosion analysis. He formerly was associated with the Engineering Test Division of Phillips Petroleum Company and with Branson Instruments, Inc. He received a BS in electrical engineering at University of Kansas. He is a member of NACE.

D. R. FINCHER is corrosion engineer for Tidewater Oil Co., Houston. He has a BS in chemical engineering from Texas A & M College and is a member of NACE.

WILLIAM A. FRAGETTA is a research metallurgist with Inco, working primarily on development of welding of high nickel alloys. He is a 1953 graduate of Rensselaer Polytechnic Institute.

HOWARD T. FRANCIS is affiliated with Continental Can Company. He has a BS in chemistry from Mount Union College and a PhD from

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BIOGRAPHIES

Pennsylvania State College. Formerly he was employed by Armour Research Foundation's Electrochemistry Section.

A. J. FREEDMAN is project engineer in the Corrosion Section, Materials Division of Engineering Research Department, Standard Oil of Indiana. Formerly, he did research work at MIT, Los Alamos Laboratory and the University of New Mexico. He has a PhD from New York University.

R. E. GACKENBACH is associated with Organic Chemicals Division of American Cyanamid Co., Bound Brook, N. J. He has a BS in metallurgical engineering from Lehigh University.

GEORGE E. GALONIAN is a corrosion chemist at the Knolls Atomic Power Laboratory, Schenectady, N.Y. He has a BS in chemistry from Siena College.

PAUL J. GEGNER is plant materials engineer for the Columbia-Southern Chemical Corp., Barberton, Ohio. His responsibilities include evaluating and specifying materials of construction and corrosion protection. He is a member of NACE.

WILLIAM R. GIBSON is development engineer at Callery Chemical Company's Research and Development Division, Callery, Pa. Formerly he was with Koppers Company and Pittsburgh Coke and Chemical before serving as an Army Chemical Corps officer. He has a BS in chemical engineering from Carnegie Institute of Technology.

HARRY GILMAN is a corrosion engineer and head of plant services in the Process Engineering Department of General Aniline and Film Corp., Linden, N. J. He was employed formerly by Piasecki Helicopter Corporation and the Kaiser Company in corrosion evaluation studies of aircraft. He has a BS from the University of Wisconsin.

W. D. GREATHOUSE is supervisor of the Materials Section, Production Research Division, Continental Oil Co., Ponca City, Okla. He is co-author of several papers on petroleum production corrosion problems, has a BS in chemical engineering from Texas Technological College and is a member of NACE and AIME.

R. P. GULLEY is a chemical engineer in the Process Engineering Department of Gulf Oil's Port Arthur refinery. He has worked on various phases of utilities engineering since joining Gulf in 1947. He has a BS in chemical engineering from Louisiana State University and is a member of NACE.

NORMAN R. HARPSTER is research associate at the Universal-Cyclops Steel Corp., where his work involves research and development of super alloys. Formerly he was research engineer with Armco Steel Corp., at the Baltimore Laboratory. He has a BS in engineering physics from Lafayette College.

GEORGE H. HERMAN is area engineer of the Chemical and Process Development Departments at Parke, Davis and Company. He received his BS in chemical engineering in 1951 from Lawrence Institute of Technology in Detroit. He is a registered professional engineer.

BERNARD HUSOCK is chief engineer of Harco Corporation's corrosion control activities. Prior to joining Harco in 1950, he did design and development work on aircraft radar equipment for Philco. He has a BS in electrical engineering from Drexel Institute of Technology.

WILLIAM IBSEN is associated with the Structural Resins Department of Ciba Products Corporation, Kimberton, Pa. He has a BS in chemical engineering from Lafayette College.

OLE G. JANSSON is a research assistant in electrical engineering at the University of Illinois and is assisting in the University's Cathodic Protection Laboratory. He graduated from the Abo Akademi University in Finland and was a research assistant there for four years. He is continuing his studies toward an advanced degree in chemistry at the University of Illinois.

HAROLD T. JOHNSON is a chemical engineer in the Metal Research and Development Division of Continental Can Co., Chicago. His work involves electrochemical corrosion in metal containers. He received a BS in chemical engineering from Illinois Institute of Technology and is author of several papers on corrosion of canned carbonated beverages.

J. E. JOHNSON is senior engineer in charge of the Underground Equipment Branch of the Electrical Engineering Division, Philadelphia Electric Co. He has been with this company since his 1930 graduation from Lehigh University with a BS in electrical engineering. A registered professional engineer in Pennsylvania, he is a member of NACE.

WAYNE A. JOHNSON is president of Corrosion Rectifying Co., Houston. A graduate of Texas College of Arts and Industries, Kingsville, he was formerly a corrosion engineer with Texas Pipe Line Company. He is a member of NACE.

HARRY J. KEELING is a consulting engineer in Los Angeles and has been engaged in cathodic protection work since 1932. He was affiliated with Southern Counties Gas Company of California until he established his own consulting firm in 1953. He received a BS and MS from California Institute of Technology and has been a member of NACE since its formation.

SARA J. KETCHAM is a metallurgist in the Surface Treatment and Corrosion Section of the Aeronautical Materials Laboratory, Naval Air Material Center, Philadelphia. A graduate of Bryn Mawr College, she was employed formerly in the Industrial Test Laboratory, Philadelphia Naval Shipyard. She is a member of NACE and ASM.

LAMBERT N. KLINGE has been working in the Materials and Corrosion Division of N. V. de Bataafsche Petroleum Maatschappij, The Hague, The Netherlands. He received a chemical engineering degree from the Technical University of Delft in 1947.

JOHN A. KNOX has been development chemist with Halliburton Oil Well Cementing Company since 1950. After receiving his BS and MS in chemistry at North Texas State College, he was head of the Science Department at East Mississippi State Junior College for four years. He also worked five years with the Western Company. He is a member of NACE, ACS and AIME.

ERNEST L. KOEHLER is director of the Chemical Metallurgy Laboratory, Central Research and Engineering Division, Continental Can Co., Chicago. He has been associated also with Gary Steel Works of U. S. Steel and Metals Research Department of the Armour Research Foundation. He has a BS and MS from Illinois Institute of Technology.

J. FRANKLIN KOEHLER is a member of the Repair Division of the Esso Standard Oil Company Marine Department, New York City. His work involves corrosion control methods for cargo tankers.

F. H. KRENZ is working on corrosion problems associated with water cooled reactors at Atomic Energy of Canada Limited, Chalk River, Ontario. He has a BS in chemistry from the University of Rochester, a MA in chemistry from the University of Toronto and a PhD from the University of Edinburgh.

W. E. KUHN is supervising engineer of the Metallurgy Department, Research and Development Division, Carborundum Company. He was employed formerly by National Lead Company and Ontario Research Foundation. He has a BS in metallurgical engineering from the University of Toronto. He is a member of NACE, Electrochemical Society, Institute of Metals (London) and AIME.

FRANK L. LaQUE is vice-president and manager of the Development and Research Division, Inco, New York City. A past-president of NACE, he has been honored for his promotion of corrosion studies and has published several technical papers here and abroad.

R. J. LAW is affiliated with the Development and Research Division of Inco of Canada Ltd. He was associated formerly with Ferro Enamels (Canada) Ltd. He has a BS in chemical engineering from McGill University and is a member of NACE, ASM and Chemical Institute of Canada.

WILLIAM LECHNICK is affiliated with the Advanced Development and Planning Department, Westinghouse Electric Corp. He was formerly with the Corrosion Group, Nuclear Division of the Martin Company and with the chemical engineering division of Argonne National Laboratory. He received his MS in chemistry from Aurora College in 1952.

J. C. LEMMON is head of Roofing Consultants, Inc. He was associated formerly with Bodwell-Lemmon Inc., and the Phillip Carey Company. He has a BS from Georgia Institute of Technology.

WILLIAM T. LINDSAY is supervisory engineer at the Bettis Plant of Westinghouse Electric Corp., Pittsburgh, Pa. He has a BS in chemical engineering from Rensselaer Polytechnic Institute and a PhD in physical chemistry from MIT. He was a research associate at MIT for two years prior to joining Westinghouse. His primary field is coolant technology of pressurized water reactors.

HUGH L. LOGAN has been associated with the National Bureau of Standards since 1936. His early work at the Bureau dealt with corrosion and stress corrosion cracking of aluminum alloys. He received a BS in chemistry from Tarkio College and a MS in physics from the University of Colorado. He is a member of NACE, ASM, Electrochemical Society and Washington Academy of Sciences.

JOHN H. LUX is president and director of Haveg Industries, Inc., Wilmington, Delaware. Formerly he was associated with Shea Chemical Corp., General Electric, Witco Chemical Co., and Atomic Basic Chemical Corp. He has a BS, MS, and PhD in chemical engineering from Purdue University.

R. B. MacQUEEN is foreman of the Builder's Department at Gulf Oil Corporation's Philadelphia refinery. He is responsible for the application of paints and protective coatings to all refinery equipment.

R. W. MAIER is corrosion engineer with Gulf's Manufacturing Department in Pittsburgh. Formerly he did research and sales work in protective coatings. He has a BS and MS in chemical engineering from the University of Pittsburgh and is a member of NACE.

BYRON E. MARSH is leader of the Petroleum Research Section, Armour Chemical Division, Chicago. His work for the past five years has dealt with the uses of fatty nitrogen derivatives in the fields of production and refining of oil and as corrosion inhibitors, bactericides and oil additives. He worked two years with the Atomic Energy Commission at Oak Ridge. He received a BA in chemistry at Illinois College in 1943.

T. P. MAY is manager of Inco's Harbor Island Testing Station. Formerly he was head of the corrosion section, Chemistry Division, U. S. Naval Research Laboratory, Washington. He is a member of NACE.

J. P. McARDLE is engaged in corrosion work with American Telephone and Telegraph Company, where he has worked since graduation from Alabama Polytechnic Institute in 1926 with a BS in electrical engineering.

D. W. McDOWELL, JR., is a metallurgist in the Stainless Steel and Heat-Resistant Alloys Section of the Development and Research Department at Inco. He is a graduate of the University of Pittsburgh with a BS. He is a member of NACE, ASM and AWS.

R. L. McGLASSON is a metallurgist in the Materials Section of Production Research of Continental Oil Co. His work deals with corrosion metallurgy. He was employed formerly by Boeing Airplane Co., Wichita, Kan. He has a BS in physics and mathematics from Northwestern State College, Alva, Okla.

JOHN W. McGREW is a plant chemist with the Solvay Process Division of Allied Chemical Corp., Baltimore, Maryland. He has a BS in chemistry from Western Maryland College. He has written several papers on the applications of chromium chemicals.

R. D. MERRICK is head of the Corrosion Research Group at Esso Research and Engineering Company. He received a BS in metallurgical engineering from Purdue University and a MS in chemical engineering from Newark College of Engineering. He is a member of NACE.

D. N. MILLER is assistant corrosion engineer for Southern Pacific Pipe Lines, Inc., Los Angeles. He received a BS in engineering at the University of Southern California in 1949. He spent two years in general engineering work and eight years in corrosion engineering.

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BIOGRAPHIES

(Continued From Page 101)

KENNETH L. MOORE is corrosion engineer at the Tidewater Oil Company refinery in Delaware. He did process design and corrosion work for three years with Atlantic Refining Company. He received a BS in chemical engineering and metallurgical engineering at the University of Michigan in 1954.

WALTER A. MUELLER is head of the corrosion laboratory at the Pulp and Paper Research Institute of Canada. He received his PhD from the University of Heidelberg, Germany, in 1934. He was corrosion engineer with a Berlin company for several years. His work has been in fundamental problems of corrosion in metallurgy and physical chemistry.

H. G. NOBLE is senior engineer with Technical Sales, Refractories Division, Carborundum Co., Perth Amboy, N. J. He joined this company's staff in 1928 as a design engineer.

S. JOHN OECHSLE, JR., is executive vice-president of Metalweld, Inc., Philadelphia. He has written several publications on the contract phase of the corrosion field.

A. W. PEABODY is an electrical engineer for Ebasco Services, Inc., New York City. Since 1939 he has been engaged in cathodic protection systems for pipe, cable and generating station facilities. He is a 1937 graduate of the University of Maine.

G. R. PEASE is supervisor of the Welding Research Section, Inco Research Laboratory, Bayonne, N. J. Formerly he was affiliated with the Ordnance Department of the U. S. Army. He has a BS and MS in chemistry from the University of Massachusetts.

J. WATSON PEDLOW is president of Quelcor, Inc., Chester, Pa. Formerly he was associated with American Viscose Corporation. He has a BS in chemistry from Dickinson College and a doctorate from the University of Munich. He is a member of NACE and ACS.

JACK E. PICCARDO is director of the Pump Technical Division of Corr-Oliver Inc. Formerly he was employed by Barnes Mfg. Co., Fairbanks Morse and Co., and Jacuzzi Bros., Inc. He received his BS from the University of California, Berkeley.

ROBERT M. PINES is leader of the Applications Group, Research Laboratories, Geigy Chemical Corp., Yonkers, N. Y. His work involves testing of corrosion inhibitors, metal chelates and surface active agents for aqueous and nonaqueous systems. He was employed formerly by Valentine Co., National Lead Co., and New York City Board of Transportation. He received a BA from Brooklyn College in 1944 and is a member of NACE, ACS, API and AATCC.

C. S. PORTER is a design engineer at Union Bag-Camp Paper Corp., where he is involved in the problem of digester corrosion. He received a BS in mechanical engineering from Purdue University in 1955.

F. A. PRANGE is affiliated with the engineering department of Phillips Petroleum Company, Bartlesville, Okla., where his work involves corrosion and metallurgical problems. He received his BS and MS in metallurgical engineering from Purdue University.

DAVID KENNETH PRIEST is manager of the applied research department, Pfaudler Division, Pfaudler-Permutit Inc., Rochester, N. Y. He has a BS, MS and PhD from Ohio State University, where he was a research associate for two years.

JOHN F. RADAVICH is assistant professor of physics at Purdue University. His fields of interest are high temperature oxidation and structure studies using electron microscope, electron diffraction and X-ray diffraction techniques. He obtained his PhD from Purdue University in 1953.

R. J. RAUDEBAUGH is head of the research laboratory, Ferrous Alloys Section, International Nickel Co. Formerly he was affiliated with Armco Steel Corporation and taught at Purdue Univer-

sity, University of Rochester, Georgia Tech and Brooklyn Polytechnic Institute.

DAVID ROLLER is a project engineer at the Wright Air Development Center, Materials Laboratory, Wright-Patterson AFB, Ohio, where his work is primarily in the corrosion field. Formerly he was employed by Freeport Sulphur Co. He has a BS in chemistry from MIT and is a member of NACE.

BOYD G. SCHULTZ is supervisory engineer at the Bettis Plant of Westinghouse Electric Corp., Pittsburgh, Pa. He is engaged in corrosion and reactor coolant control work. He was employed formerly by Tennessee Eastman Corp., Oak Ridge. He has a BS and PhD in chemistry from the University of Wisconsin.

JOHAN SELMAN is in the Technical Information Section of the Oil Development Department of N. V. de Bataafsche Petroleum Maatschappij, The Hague, The Netherlands. He is a graduate of The Higher Technical School of Amsterdam.

D. E. SIMMONS is an electrical engineer with the Houston Lighting and Power Company, where he is involved in corrosion control work. He received a BS in electrical engineering from Rice Institute in 1947.

E. N. SKINNER, JR., is affiliated with Inco, where his activities have been in the area of alloy selection from various types of high temperature service. He has a PhD in metallurgy from Yale University.

ARTHUR B. SMITH is southeastern district manager of Amercoat Corp. Former chairman of the NACE Southeast Region and Jacksonville Section, he has been connected with corrosion control work for 14 years.

YALE SOLOMON is an engineer at the Bettis Plant, Westinghouse Electric Corp., Pittsburgh. Formerly he worked at Argonne National Laboratories. He has a BS in chemistry from Roosevelt University and a MS in physical chemistry from Illinois Institute of Technology.

JOHN D. SPIVACK is a group leader in the Organic Research Laboratory, Geigy Chemical Corp., Yonkers, N. Y., where his work involves compounds for use as corrosion inhibitors, metal chelates and surface active agents. Formerly he was affiliated with Tidewater Oil Company. He has a PhD from McGill University and is a member of ACS.

W. M. SPURGEON is supervisor of the Physical Chemistry Unit of General Electric's Flight Propulsion Laboratory Testing Division. Formerly he was employed by the Texas Company and American Fluresit Company. He has a BS in chemistry from the University of Illinois and a PhD in physical from the University of Michigan.

ROY STOUT is in charge of the corrosion group at Halliburton Oil Well Cementing Co., Duncan, Okla. He joined the company in 1954. He has a BS from Harding College and received a MS in chemistry from Texas A & M College in 1954.

TED M. SWAIN is technical service representative for Solvay Process Division, Allied Chemical Corp. Formerly he was engaged in corrosion control chemical sales. He has a BS in chemical engineering from Pennsylvania State University.

JAMES A. THOMPSEN is marine sales engineer for the American Hard Rubber Company. He is a graduate of the Merchant Marine Academy and City College of New York. He has written several papers on marine corrosion.

G. F. TISINAI is project supervisor in the Metals Section, Materials Division of the Engineering Research Department, Standard Oil Co., Whiting, Indiana. He has a BS from the University of Illinois and a MS in metallurgical engineering from Illinois Institute of Technology.

E. S. TROSCINSKI is research engineer in the Corrosion Section, Materials Division, Engineering Research Department, Standard Oil of Indiana. Formerly he was employed by U. S. Rubber and Corn Products Refining Co. He has a BS in chemical engineering from the University of Illinois.

H. H. UHLIG is head of the MIT Corrosion Laboratory, where he began corrosion research in 1936. A graduate of Brown University, he received his PhD at MIT. He has published

papers on corrosion and is editor of the "Corrosion Handbook." He received the 1951 Willis R. Whitney Award of NACE for contribution to the science of corrosion.

KENNETH H. VOGEL is supervising engineer of the Irradiations Chemistry Group, Bettis Plant, Westinghouse Electric Corp., Pittsburgh. He has a BS in chemical engineering from Cornell University, a MS in physical chemistry and a DSc, both from Carnegie Institute of Technology.

V. B. VOLKENING is group leader in the Materials Evaluation Laboratory, Chemical Engineering Department, Texas Division of Dow Chemical Co., Freeport. He has a BS in chemical engineering from the University of Texas and is a member of NACE, ACS and American Wood Preservers Association.

J. R. WELLINGTON is research engineer with the Metal Use Research Group, Research and Development Division of Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C. His group specializes in corrosion studies and new product development. He has a BS in chemical engineering from the University of Saskatchewan and is a member of NACE and ASTM.

ROY P. WHITNEY is dean and vice-president of the Institute of Paper Chemistry, Appleton, Wisconsin. Formerly he was professor of chemical engineering at the University of Maine and assistant professor at MIT. He has a BS, MS and DS in chemical engineering from MIT.

W. L. WILSON is a senior research chemist in the Barberton Laboratories of Columbia-Southern Chemical Corp., where he has been engaged in corrosion work for six years. He was formerly employed by Belle Alkali Co. He has a BS in chemical engineering from West Virginia University and is a member of NACE.

W. E. YOUNG is a research engineer, Westinghouse Research Laboratories, engaged in combustion and thermodynamic research for industrial gas turbines. He has a BS in mechanical engineering from the University of Vermont and a PhD in mechanical engineering from the University of Pittsburgh, where he is also a lecturer. He is a member of ASME and NACE.

Publication Procedure
For Conference Papers

Technical papers presented at meetings of the National Association of Corrosion Engineers, will, after review and approval by the NACE Editorial Review Subcommittee and the editor of CORROSION be published in the Technical Section of the magazine. Persons interested in the material thereby will have access to the information in CORROSION, which is extensively indexed both by NACE itself and by other agencies.

Corrosion workers concerned with technical literature originating with and published by NACE are invited to write to the association for copies of the NACE Literature List.

The association does not publish a proceedings of its meetings. Publication of technical papers usually follows their presentation by periods of months, because of the time consumed in review, editing and revision. The association also considers for publication technical articles submitted without invitation on any phase of the corrosion control problem.

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A total of 16 symposia is scheduled during the Chicago Conference.

GENERAL NEWS

NACE to Give Advice On API Short Course

A committee of NACE members is giving technical advice to a group from the American Petroleum Institute formulating a short course on corrosion of oil and gas well equipment probably to be given by the University of Oklahoma. The course will be similar to other API short courses. NACE's contribution is similar to that given in the preparation of the API corrosion manual published in September.

The committee formulating the course met first November 20 to prepare a general outline to be followed in the course.

Designed for field operating personnel, the course is proposed to increase the appreciation of the enormous cost of oil field corrosion, improve ability to recognize early indications of corrosion, to stress the importance of early reporting and to improve the desire of personnel to take an effective part in the solutions of corrosion problems.

Practical work included in the course will familiarize students with the use of coupons to determine the nature and severity of corrosion and with some of the field methods for determining iron content. Various soil bank tests will be included.

The course will first be developed, tested on a pilot group and then scheduled as requests are received. Classes are held in the various oil centers throughout producing areas. Instructors are usually members of extension divisions of state colleges and universities.

NACE members working with API are J. P. Barrett, Pan American Petroleum Corp., Tulsa, W. C. Koger, Cities Service Oil Co., Bartlesville, Okla., F. Prange, Phillips Petroleum Co., Bartlesville and J. D. Sudbury, Continental Oil Co., Ponca City, Okla. J. R. Hatfield, Cities Service Oil Company, Bartlesville, is general chairman of the committee organizing the course.

Russian Progress

Interesting possibilities are found in the Russian development of highly ductile tungsten, according to Claus G. Goetzel of New York University in a report of his inspection tour of Russian powder metallurgy facilities.

The Russians have also made good progress in powder metallurgy techniques for titanium and beryllium, he reports. Their research and development work is both advanced and intensive.

Plastic Engineers Meet

Fifteen Annual Technical Conference of the Society of Plastic Engineers will be held January 27-30, Hotel Commodore, New York City.

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Over 100 companies will have exhibits in 140 booths at the 1959 Corrosion Show in Chicago, March 17-19.

College-Industry Panel Planned for Jan. 26-27

An exchange of ideas between engineering educators and representatives of industry will be promoted at the annual College-Industry Conference to be held January 26-27 at the University of Houston, sponsored by the American Society for Engineering Education.

Conference theme will be Industry Speaks Its Mind on Engineering Education. Panel discussion topics are (1) Scientific vs Practical Approach to Engineering Education, (2) The Team Concept in Engineering, (3) Federal, Corporate and Private Support of Engineering Education and (4) Obsolescence in Engineering.

Additional information can be obtained from Clanton W. Williams, President, University of Houston or Joe T. Dickerson, President, Shell Pipe Line Corp., Shell Bldg., Houston 2.

Purdue University to Hold Packaging Short Course

A short course on industrial packaging will be held at Purdue University March 2-13. New developments in the packaging field and corrosion and deterioration related to military packaging will be included.

Additional information can be obtained from Division of Adult Education, Memorial Center, Purdue University, Lafayette, Indiana.

AIME January Conference

Three papers of probably interest to corrosion engineers are scheduled during the first conference of the Mechanical Working Committee of AIME to be held January 21 in Chicago.

Titles of the papers are Continuous Normalizing of Flat Rolled Products, Continuous Strip Annealing and Continuous Coil Annealing. The papers are part of the symposium on Continuous Heat Treatment of Flat Rolled Products.

Paint and Varnish Club

Miss Naomi Ekman, teacher at Houston's Austin High School, evaluated a short paint course she attended at North Dakota University for the November meeting of the Houston Paint and Varnish Production Club. She explained how she intends to stimulate student interest in the coating industry.

Reactor Design Accepted

A design study by Sargent & Lundy, Chicago, has been accepted by the Atomic Energy Commission for a heavy water moderated nuclear power plant.

An evaluation is to be made to determine the optimum plant concept and size. This type reactor is considered potentially capable of producing economic nuclear power.

Appalachian Short Course Set June 2-4

June 2-4 has been set as the dates for the 1959 Annual Appalachian Underground Corrosion Short Course to be held at the University of West Virginia School of Mines in Morgantown.

Endorsed by NACE, the course covers both technical and non-technical presentations of the practical and theoretical aspects of corrosion.

The short course dates were set by the General Committee at its December meeting held in Philadelphia.

Members of the committee are General Chairman Charles L. Dey, Koppers Co., Inc., Pittsburg; Publications Chairman T. S. Watson, Socony Mobil Oil Co., Inc., Plainfield, N. J.; Registration Chairman and School Secretary Ross E. Hanna, Jr., West Virginia University; Exhibits Chairman George E. Campbell, University of West Virginia; Program Chairman Charles M. Rutter, Jr., Equitable Gas Co., Pittsburgh; and Publicity Chairman John H. Alm, Dearborn Chemical Co., Pittsburgh.

General chairman for the 1958 short course was Carl A. Erickson, Peoples Natural Gas Co., Pittsburgh.

Exhibit space for the short course can be arranged through George G. Campbell at the University of West Virginia.

Building to Honor Scientist

The new chemistry building at the University of Buffalo has been named the Edward Goodrich Acheson Hall of Chemistry as a memorial to the inventor-scientist who formed the Carborundum Company in 1891.

He invented the diamond-like abrasive which he called Carborundum and also developed chemically pure, man-made graphite. He died in 1931.

Federal Bulletin Published

The first in a new bulletin series listing all significant scientific information sources or activities within the federal government is being published by the National Science Foundation, Science Information Service, Washington 25, D. C.

Air Pollution Report Needed

Guesswork and duplication could be eliminated from air pollution research if a world-wide catalog of tiny pollutant particles found in the air were available, according to Albert F. Bush, University of California. Compiled by microscopists, the catalog would show sizes and concentrations of particles in all countries plus identification of the source, such as generating plant smoke, incinerators and auto exhaust.

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Over 70 technical committees will meet during the 15th Annual NACE Conference in Chicago.

NEW PRODUCTS

Equipment Services   **Materials Literature**

Aluminum

An All-Aluminum Hangar is being built by Reynolds Metals Company, Richmond, Va., to house company aircraft. Overall dimensions of the structure are 165 by 108 feet.

Atomic Energy

A Low Power Reactor, New York States' first privately owned, is in operation at the Pawling Laboratories at White Plains, part of the Nuclear Development Corporation of America. The low power reactor is a prototype of a teaching and research reactor developed by NDA for university use.

Cleaning

Steam Cleaner Units have been installed on 28 trucks by the Clayton Mfg. Co., 401 North Temple City Blvd., El Monte, Cal., for portable units. The 280 Blast-Master units can fire up in one minute, according to the manufacturer.

Coatings

The Sheldon Company, 350 Lexington Ave., New York 16, has been appointed to handle sales and service for the Niphos nickel-alloy coating process of the Tube Reducing Corp.

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A New Technical Bulletin titled "Liquid Polymer-Epoxy Resin Systems" is available from Thiokol Chemical Corp., 780 North Clinton Ave., Trenton 7, N. J. It is designed as a basic reference manual for plastics compounders.

Consolidations

Enthone, Inc., of New Haven, Conn., is taking over and continuing its subsidiary Comco, Inc., which has specialized in the engineering, design and manufacture of metal finishing equipment and fabrication of corrosion resistant plastic tanks and exhaust casings for the chemical process industries.

Filters

A New Dax System for cleaning and adhesive application of electronic air cleaners has been announced by Electro-Air Cleaner Co., Inc., Olivia and Sproul Streets, McKees Rocks, Pa. It is designed to eliminate the collected contamination on electrodes and plates of collecting cells.

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Dust is being removed from the Dragon Cement Co., Northampton, Pa., by aerostatic dust collectors made by Hagan Chemical & Controls, Inc., P. O. Box 1346, Pittsburgh 30. Installed on clinker coolers, the collectors remove a daily average of 9500 pounds of re-usable product.

Fume Washers

A Fume Washer made of solid plastic has been manufactured by Heil Process Equipment Corp., Cleveland 11. Twelve feet high with a seven-foot outlet, it was constructed of a special epoxy formulation reinforced with glass fiber designed for handling and scrubbing chemical corrosive fumes.

Instruments

A New Bulletin is available from Newage Industries, Inc., 222 York Road, Jenkintown, Pa., which describes a new microhardness tester that permits direct readings within 15 seconds by measuring resistance hydrostatically. Microscope, conversion charts and tables are eliminated by the tester.

Mufflers

Mufflers designed for longer service under extreme conditions of temperature and corrosion are being manufactured by Alexander-Tagg Industries, Inc., Hatboro, Pa. Made of chrome diffused steel, they have resisted temperatures to 1700 F, according to ATI.

Plants

Johns-Manville has opened a new Dutch Brand Division plant in south Chicago. One of eight new plants, it will produce pressure sensitive tapes, adhesives and related rubber products.

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Walter Weyman Co., distributor of protective coatings, hoists, cranes, monorails, conveyors and other industrial equipment, has moved into new plant facilities at 607 Addison Street, Berkeley 10, Cal.

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Pittsburgh Coke & Chemical Company is supplying fumaric acid used in making plastics, paints and chemicals produced at the new plant at Neville Island, Pa.

•

Union Carbide has purchased Amoco Chemicals' plant at Brownsville, Texas. The plant was used to produce synthetic gasoline, other petroleum fractions and co-product chemicals from natural gas by the Fischer-Tropsch process. Union Carbide has announced it does not intend to produce these products.

Non-Metallics

An Illustrated Bulletin describes the carbon, graphite and impervious carbon and graphite equipment for chemical processing applications available from National Carbon Co., 535 Fifth Avenue, New York 17.

•

Quick Setting Silicone Rubber will vulcanize in 30 minutes at room temperature, according to Dow Corning Corp., Midland, Michigan, maker of Silastic RTV 502. It is recommended for sealing and caulking metal-to-metal and metal-to-rubber joints and as a shock and vibration absorber for delicate components.

Periodicals

A News Sheet of current information on cryogenics and related subjects called "Kelvin Scale" will be published periodically by Arthur D. Little, Inc. Copies can be obtained from the Editor, 20 Acorn Park, Cambridge, Mass.

Plastics

Polyethylene Pipe with greater initial burst strength has been introduced by Union Carbide Plastics Co. The manufacturer claims the pipe features corrosion resistance, low temperature properties, flexibility for coiling, light weight and resistance to environmental stress cracking.

•

A Water Conditioning Tank made of centrifugally molded fiber glass has been developed by Apex Reinforced Plastics, Cleveland. Manufactured in a variety of diameters, the tank offers weight savings over steel and alloys and resistance to corrosion, chemical action and impact.

•

Applications of a new thermoplastic with mechanical and chemical resistant properties called Penton are described in a brochure available from the Hercules Powder Co., Wilmington 99, Delaware.

•

Large Diameter Pipe is being produced from polyethylene by Allied Chemical by a new extrusion technique and die design. The pipe is available from Carlon Products, Corp., Aurora, Ohio.

•

A Rigid PVC Expansion Joint which is fully guided when extended is being produced by Walworth Co., 750 Third Avenue, New York City. Maximum traverse of the joint is four inches.

•

Heat Effects on plastic laminates are being studied by Taylor Fibre Co., Norristown, Pa., in a new electric oven which can produce temperatures to 1000 F.

MEN in the NEWS

John R. Smith, former corrosion engineer for Dowell, has joined the Tretolite Company as corrosion engineer in the south Louisiana district. A member of NACE, he received his BS from Louisiana State University. **Mike C. Deodati, Jr.,** also a NACE member, will represent Tretolite in the Houston area. **Ed L. Dressel,** head of the company's field service laboratory at Odessa, has been transferred to the sales department as a corrosion engineer for the West Central division. **Robert W. Taylor,** a technician in the St.

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MEN in the NEWS

(Continued From Page 104)

Louis laboratory, has been named junior testing engineer and will replace Dressel at Odessa.

John F. Howe, Jr., has been named sales manager of Industrial Finishes Co., Philadelphia. He was formerly with Sherwin-Williams Company.

William H. Smith has been appointed manager of the newly formed Product Finishes Department of Allied Paint Mfg. Co., Tulsa.

Robert Allan is the sales representative in the Detroit area for Wolverine Tube. He was replaced in the Grand Rapids area by Jack Gavigan.

Alejandro Fuenmayor Sotillo of Caracas has been appointed Venezuelan sales representative for Tubular Lining Corp., Houston.

H. C. Van Nouhuys has organized Corrosion Mitigation, Inc., 908 Boulder Crest Drive, Marietta, Ga. The company will design and engineer cathodic protection systems for transmission, distribution and industrial applications. Mr. Van Nouhuys is a NACE member.

M. G. Fontana and Mrs. Fontana spent six weeks in Europe this summer and visited the corrosion exhib't in the Metallurgy Building at the Brussels World Fair which included cathodic protection, corrosion testing and a display of eight forms of corrosion.

Bob Churnside, sales engineer for F. H. Maloney Co., is in charge of a new sales district covering the Chicago area. His office is 710 East 10th Street, Michigan City, Ind.

James A. Green has been appointed sales representative for Tubular Lining Corp., Houston.

Merritt L. Smith is director of advertising and publicity for Metal & Thermit Corp.

Edgar H. Dix, Jr., retired assistant director of research for the Aluminum Company of America, has been awarded the Distinguished Public Service Award for his contributions to the Navy in the fields of scientific research and development. He is a member of NACE.

George Roberts has been appointed field manager of the Safe-T-Clad Products Division of Seamless Rubber Co., New Haven 3, Conn.

William M. Freeman is the new manager of the process equipment sales group at Chicago Bridge & Iron Company, with headquarters in New York City.

L. B. Swan has been promoted to vice-president of the Dowell Division of Dow Chemical Company. With his office in Houston, he will be responsible for Dowell's foreign operations.

Frank K. Pittman has been appointed director of the AEC Division of Reactor Development.
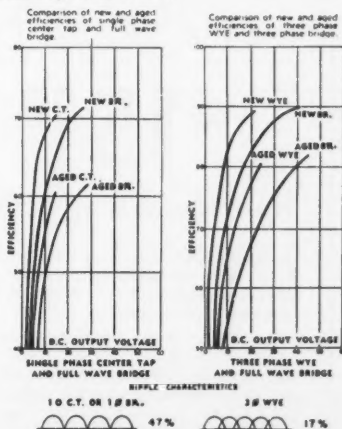
A Summary of 45 Years Of NBS Research

Underground Corrosion*

Figure 1—Similar corrosion patterns on different wrought metals exposed to the same soil (Hempstead silt loam) for approximately 12 years. Examples shown are A: open-hearth iron; D: wrought iron; K: open-hearth steel; M: Bessemer steel; and Y: open-hearth steel with 0.2 percent copper.

Abstract

The National Bureau of Standards' underground corrosion investigations since 1910 are summarized briefly. Some of the discoveries growing out of these researches are enumerated and the principal causes of corrosion discussed. Results of the burial tests on metals, coatings and wrappings and asbestos-cement pipe are given.
4.5.1

RESEARCHES by the National Bureau of Standards on the corrosion of underground structures, carried on for over 45 years, have been marked by steadily improved understanding of the casual factors at work and by the development of increasingly effective means of preventing the harmful effects that underground corrosion produces.[1] An important phase of the work, now essentially complete, has been an extensive field-burial program to determine the specific behavior of metals and coating materials when exposed for periods up to 17 years in a wide range of soil environments. At the same time, other phases of the corrosion program have led to increased information on the electrical and chemical aspects of the corrosion process, development of methods and instruments for measuring soil characteristics, improvements in the technique of cathodic protection and virtual elimination of corrosion due to stray-current electrolysis.

There are now in this country about one million miles of gas, water and oil pipelines; 170,000 miles of buried power and communication cables, and an unknown number of tanks, pilings, burial vaults and other structures. The annual cost to the U. S. pipeline industry alone, for protective measures and replacements due directly to corrosion, is estimated at $600 million. A still higher indirect cost results from loss of products, service shutdowns and loss of life and property by explosion and fire due to leakage from corroded pipes. Furthermore, since corrosion rates are often unknown, engineers have wasted large

★ Summary Technical Report 2209, National Bureau of Standards, Washington 25, D. C.

NBS Research

Current research on corrosion at the National Bureau of Standards emphasizes basic processes and principles. Two of the important current projects are conducted in cooperation with the Corrosion Research Council in its efforts to increase emphasis on the basic principles underlying corrosion. Since completion of the work described in the accompanying article, field studies have been confined to a few of the newer metals and alloys, such as titanium, stainless steels, copper-nickel alloys and aluminum alloys that have come into use recently for underground structures.

Basic studies include further investigation of current and potential relationships, electrochemical polarization and other electrical phenomena associated with corrosion. The chemistry of corrosion continues to receive major attention. One such study deals with the effects of adsorbed layers of moisture, presence of carbon dioxide, intensity of illumination and other factors on corrosion reactions at the metal surface. Another study, part of the larger program on free radicals under way at the bureau, is concerned with the effect of atomic oxygen on metals at low temperatures.

A somewhat different approach is the investigation of corrosion in large single crystals. By such experiments a start has already been made in correlating corrosion with the arrangement of atoms in the crystal lattice. The importance of crystal structure also has appeared in work on stress-corrosion cracking, a particularly damaging type of failure resulting, as its name suggests, from the combined effects of stress and corrosion.

By attacking the problem from these various directions, it is hoped not only to improve still further the methods of combating corrosion, but to obtain information on basic properties of matter that have even wider areas of application.

quantities of material by specifying unnecessarily large thicknesses in their designs.

Until about 35 years ago, underground corrosion was attributed solely to stray electric currents from external sources such as dc powerlines and electric railways. Such currents pass through parts of underground structures and then discharge to the earth where conditions are favorable; corrosion occurs at the discharge areas.
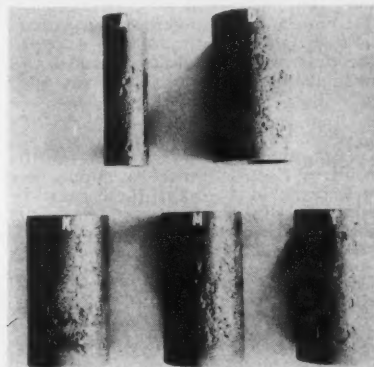
Authorized in 1910

The seriousness of the problem was recognized by the Congress in 1910, when the bureau was authorized to investigate the corrosive effects of stray currents and methods for combating them. In 10 years of field and laboratory studies, methods were developed that eliminated stray-current electrolysis as a major factor in underground corrosion.[2] Unexpectedly, however, these studies also showed that serious corrosion often occurred when stray currents were absent.

In 1922, therefore, a field burial program was initiated to determine the influence of various properties of soils on the corrosion of buried metals and to develop further methods for reducing corrosion losses. Data were obtained on nearly 37,000 specimens representing 330 varieties of materials. These were exposed for periods up to 17 years in 95 different types of soil at 128 test sites throughout the United States. The last specimens were removed in 1952 and several more years were required to analyze the data. The major field-burial program is now terminated; present work is confined to newly developed materials and the completion of several unfinished studies.

Meanwhile, electrical and electrochemical aspects of underground corrosion were continuously studied in the laboratory. The differential aeration cell developed by I. A. Denison and modified by his co-workers, has been used to compare the corrosivities of different soils and of different metals in the same soil. Studies by W. J. Schwerdtfeger showed that the instantaneous rate of corrosion for ferrous metals in soils could be determined quantitatively from polarization characteristics of the metal.

Inspection Code Adopted

By-products of the investigation include a widely adopted inspection code for pipes and coatings and the development of methods and instruments for measuring the electrical resistivity of

Underground—

soils in the field, such as the McCollum Earth Current Meter, the Wenner Four-Terminal Method, the Megger and the extensively used Shepard Canes.

In the course of the field investigations, the bureau had the cooperation of 17 technical and Government organizations, 103 manufacturers who supplied materials, and 105 utility companies and municipalities that provided test sites and labor.

Causes of Corrosion

Most underground corrosion is the result of electrochemical reactions. For such reactions to occur there must be a potential difference between two points of the metal in contact with an electrolyte. Current flows from the anode area

through the electrolyte to the cathode and returns through the metal to complete the circuit. The anode area corrodes through loss of metal ions to the electrolyte.

Although this theory is easily understood, correlation of the theory with actual corrosion of metals underground is complicated because of the many factors that determine not only the amount or rate of corrosion, but also whether it is uniformly distributed over the metal surface, or is localized as the pitting type of corrosion. The pitting type of corrosion is especially damaging in pipelines and other structures that store or carry fluids; but for load-bearing structures, such as piles, the main concern is with over-all loss in weight or strength.

The chief contributing factors are the presence of moisture, oxygen and soluble salts in the soil and the permeability of the soil to these substances. Moisture provides the soil electrolyte which is composed of hydrogen and hydroxyl ions from the water itself and variety of ions from the salts dissolved from the soil. These ions determine the electrical resistivity, as well as the chemical properties of the soil. Oxygen, from the air or from oxidizing compounds in the soil, stimulates corrosion by combining with metal ions. If the resulting corrosion products are soluble or otherwise removed from the anodic areas, corrosion proceeds; if they accumulate, they may protect the metal against further corrosion or, if they are more cathodic than the bare metal, they will accelerate and localize the corrosion.

Other factors which determine the amount of current that flows from metal to soil are the size, number and location of anodic areas. Galvanic corrosion may result because of contact between dissimilar metals and because of local differences in the packing of the soil which may produce oxygen concentration cells; the regions with less oxygen are anodic with respect to those with more.

Bacteria must also be considered, particularly the anaerobic sulfate-reducing bacteria that converts soluble sulfates to sulfides. These are most active in poorly aerated swamp areas where the pH of the soil water is about neutral and there is enough organic matter and soluble sulfates for the organisms to thrive.

Soils and Burial Procedure

The 95 soil types used in the field program show wide differences in physical and chemical properties. In texture, the soils vary from soft, spongy peats through soft clay, loams and silts to coarse-grained sands and gravels. The resistivity ranges from 51 ohm-cm, approximately that of sea water, to a value over 1000 times larger, indicating the absence of soluble salts. Chemically, the soils range from extreme acidity (pH = 2.6) to high alkalinity (pH = 10.2), and from highly oxidizing to definitely reducing. In addition, there are striking differences in the kinds and amounts of soluble salts present.

In the first extensive burials (1922), specimens of commonly used ferrous pipe materials were buried at 47 test sites. In 1928, similar ferrous materials and some copper and copper alloys were buried in a new group of sites; and a burial program was also started on bituminous coatings. Between 1932 and 1941 additional burials were made of low- and high-alloy irons and steels, copper and copper alloys, zinc, alloys of lead, lead-coated steels, galvanized iron, tin-coated copper, various nonbituminous organic coatings and asbestos cement pipe.

As a rule, 10 or 12 specimens of each material were buried at each site, and two specimens were removed periodically, so that corrosion data were obtained for maximum exposure of 12 to 17 years for all materials. Specimens were usually placed in a single row and were arranged so that two samples of each material could be removed without disturbing the specimens still in the ground. Exhumed specimens were treated in the bureau's corrosion laboratory by chemical and mechanical procedures to remove the corrosion products without significant loss in weight

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or mechanical injury to the uncorroded metal. Measurements of weight loss and pit depth were then made.

Plain Ferrous Metals

The plain ferrous pipe materials represented in the field tests were open-hearth iron and steel, hand-puddled and mechanically puddled wrought iron, Bessemer steel, plain carbon steel, pit cast and centrifugally cast iron.

The field test results for these metals, as well as those for low-alloy steels, exhibit very clearly the controlling influence of the soil on the character of the corrosion. All the plain ferrous materials showed similar corrosion patterns when buried in the same soil, but the type of corrosion varied widely in different soils as shown in Figures 1 and 2. In general, a high initial corrosion rate decreasing after a few years to almost complete cessation is found in well drained soils with high resistivities; while the corrosion rate is nearly constant after the first year or two in poorly drained soils with low resistivities.

Alloy Steels and Irons

Data were obtained on the following low-alloy steels: Copper-bearing steel, copper-molybdenum open-hearth iron, nickel-copper steels, and steels containing from 1 to 6 percent chromium with and without molybdenum.

The general effect of the alloying elements was to lower the initial rate of weight loss, but to increase the initial rate of pitting, as compared with plain carbon steel. Except in very poorly aerated and reducing soils, however, the pitting rate diminished more rapidly for the alloy steels than for plain steels. Chromium and molybdenum were particularly effective in reducing the corrosion of low-alloy steels in the most corrosive site, a cinder fill.

The higher-alloy steels tested contained up to 18 percent chromium, with and without nickel and molybdenum. Increasing the chromium content caused a gradual decrease in weight loss, but pitting was accelerated by additions of chromium beyond 6 percent. The tendency of high concentrations of chromium to accelerate pitting appears to be neutralized by adding sufficient nickel to produce steels of the austenitic type.

Field tests on low-alloy cast irons, containing up to 3 percent of nickel with and without copper, showed that the presence of such amounts of nickel or copper had no significant effect in any of the soils up to the amounts used. Austenitic cast iron was considerably more resistant to corrosion than plain cast iron.

Copper, Brass and Lead

Results on copper and copper alloys indicate that tough-pitch copper, deoxidized copper, copper containing up to 3 percent of silicon with and without tin and red brass (15 percent Zn) all behave essentially alike. Soils, including cinders, with high concentrations of sulfides, chlorides, or hydrogen ions were found the most corrosive toward these materials.

The corrosion rate of Cu-Zn alloys with more than 27 percent zinc increased approximately as the amount of zinc and was generally accompanied by dezincification—except in soils with moderate or high concentrations of sulfide. In the

sulfide soils the corrosion rate decreased with greater zinc content and dezincification did not occur.

Chemical, antimonial and tellurium lead showed no appreciable differences in corrosion behavior. The corrosion rate of each tends to increase with decreasing aeration of the soil. Organic acidity was corrosive; but in soils high in sulfates, chlorides or carbonates, the corrosion products formed a protective coating.

Metals Compared

To compare the corrosive resistances of plain iron and steels, copper, lead and zinc, the soils were divided into 4 groups: Well aerated, poorly aerated, alkaline and high in sulfide or sulfate. When corrosion-time curves were plotted for specimens buried in representative soils of these types, it was found that plain iron or steel corroded much more rapidly than the other metals in all the soils except the one high in sulfate. In this soil zinc corroded more than steel; but only lead could be expected to withstand for long the corrosive action of such a soil.

In the well aerated and poorly aerated soils which are representative of most of the United States, copper showed the highest corrosion resistance. This superiority is especially marked in the poorly aerated environment, where the corrosion rates of iron or steel, zinc and lead are proportional to time. In the well aerated environment, the rates of corrosion of the same metals de-

SOIL 51

SOIL 53

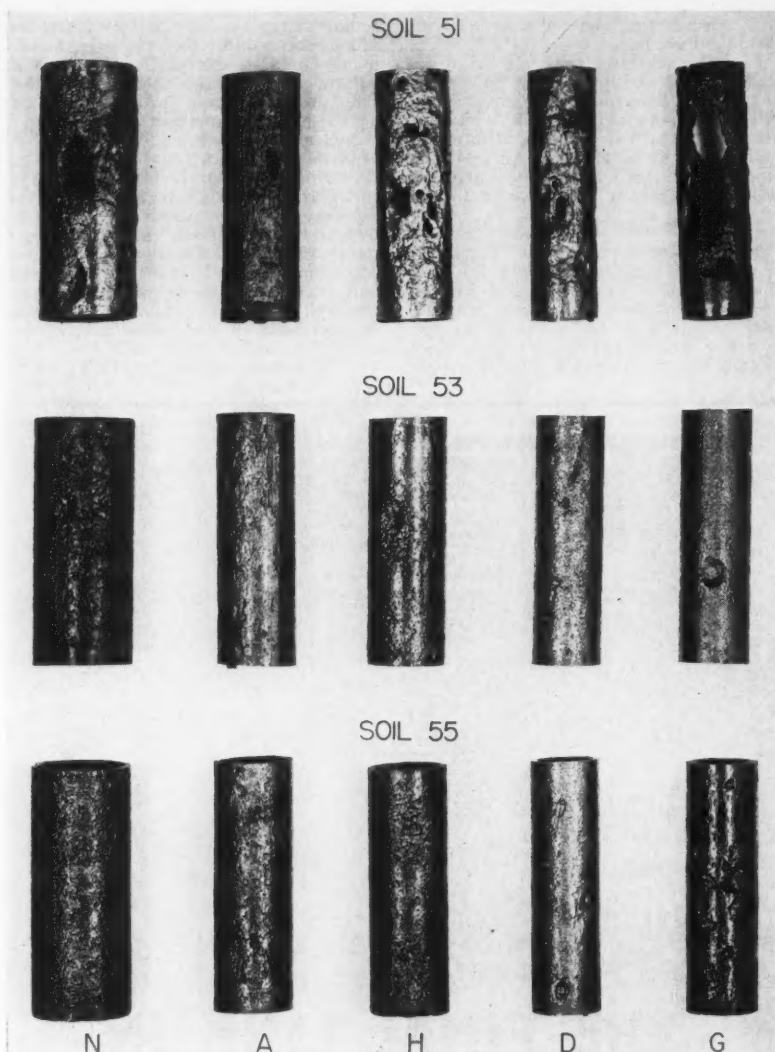SOIL 55

N   A   H   D   G

Figure 2—Corrosion patterns on five metallic specimens exposed for 14 years to three different soils. The soils used were Soil 51: highly corrosive Acadia clay at Spindletop, Texas; Soil 53: moderately corrosive Cecil clay loam at Atlanta, Georgia; and Soil 55: Hagerstown loam at Loch Raven, Maryland. Note the similar corrosion patterns produced in different metals by the same soil. The metals shown are A: wrought iron; H: copper-molybdenum open-hearth iron; D: 2-percent nickel, 2-percent copper steel; and G: plain cast iron.

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creased rapidly with longer periods of exposure.

Coatings, Asbestos-Cement Pipe

Field tests on galvanized coatings over iron and steel showed that a 2-oz/ft^2 coating of zinc was sufficient protection in inorganic oxidizing soils, 3-oz/ft^2 was needed in inorganic reducing soils, and still heavier coatings in high reducing organic soils. For steel coated with lead and copper coated with tin, both by the hot-dip process, it was found that in a great many soils the local corrosion is much deeper than the thickness of generally available commercial coatings.

Coatings of vitreous or porcelain enamel revealed no signs of deterioration in 14 years' exposure. Baked phenolic coatings showed marked superiority to air-dried phenolic coatings in preventing pit formation in the underlying steel. Rubber and rubber-like coatings were also very successful, mainly because of their large thicknesses. Numerous other organic coatings failed to give adequate protection because of insufficient thickness or unsatisfactory bonding between metal and coating.

Extensive field tests were made on all bituminous coating materials commercially available (1929-1932), including shields, wrappings and reinforcing materials. As a result of these experiments, performed with the cooperation of the American Gas Association and the American Petroleum Institute, improved methods of applying the coatings were developed, many previously used coatings were removed from the market and new specifications for bituminous coatings were adopted by the industry.

Pipes of asbestos-cement, now widely used for transporting water, were exposed for periods of up to 13 years. In general, the data show an increase in strength during the first few years, a result due to the curing process that cement products normally undergo in moist atmospheres. However, after completion of this curing period there was a loss in strength, a decrease in apparent specific gravity, increased water absorption and some softening of the surface. These effects were accelerated by both organic and inorganic acidity in the soils.[3]

Cathodic Protection

Since the early 1930's, the method of cathodic protection has come into more and more extensive use as an alternative or supplement to protective coatings. The method consists in impressing electromotive forces on the underground structure so that the entire structure remains cathodic to the soil at all times. This prevents positive metal ions from passing into solution, and thus blocks the corrosion reaction.

If electric power is available, it is converted to direct current (if not already in that form) and auxiliary anodes of scrap iron, graphite or other materials are used to carry the current into the earth. Where power is not easily available, aluminum, magnesium or zinc are used as sacrificial anodes to supply the needed emf by galvanic action.

Experimental and theoretical investigations by the corrosion laboratory have contributed to cathodic protection techniques since its early development. For example, studies were made that helped determine which soil conditions are favorable for the use of zinc sacrificial anodes.

Additional References

Some additional articles in the general area covered by these studies by workers at the National Bureau of Standards have been published as follows in CORROSION:

Geometrical Factors in Electrical Measurements Relating to Corrosion and Its Prevention. By W. J. Schwerdtfeger and Irving A. Denison. *Corrosion*, 11, No. 10, 423-432 (1955) Oct.

Electrical Measurements in the Selection of Bolt Materials for Service Underground. By W. J. Schwerdtfeger. *Corrosion*, 10, No. 10, 355-363 (1954) Oct.

Corrosion of Nickel Cast Iron in Soils. By Irving A. Denison and Melvin Romanoff. *Corrosion*, 10, No. 6, 199 (1954) June.

Effect of Exposure to Soils on the Properties of Asbestos-Cement Pipe—Final Report. By Melvin Romanoff and Irving A. Denison. *Corrosion*, 10, No. 5, 169 (1954) May.

Corrosion of Galvanized Steel in Soils. By Irving A. Denison and Melvin Romanoff. *Corrosion*, 9, No. 4, 132-140 (1953) April.

Corrosion of Low-Alloy Irons and Steels in Soils. By Irving A. Denison and Melvin Romanoff. *Corrosion*, 9, No. 4, 141 (1953) April.

Progress Report on the Behavior of Zinc-Iron Couples in Soils. By Melvin Romanoff. *Corrosion*, 1, No. 2, 95 (1945) June.

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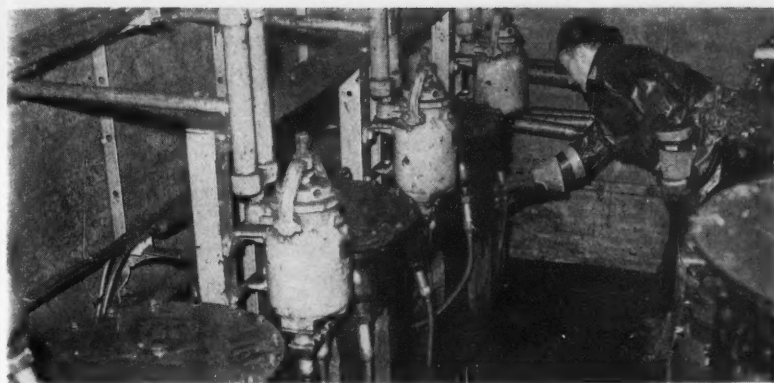rubber
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★ From
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Figure 1—Underground vaults, always damp and frequently flooded, are tough on transformer paint.

Rubber-Base Transformer Finish For Severe Environments*

FOR FIVE years General Electric's Transformer Division has experimented with and field tested a resin-modified chloroprene rubber paint (Melaprene) for transformers in corrosive locations such as underground vaults subject to frequent flooding. Some idea of the environment in which these transformers are exposed is seen in Figure 1.

The test finish consisted of a red alkyd-melamine primer, two coats of rubber-base paint and one coat of an ASA 24 dark grey alkyd-melamine finish. Transformers so coated were placed in extremely corrosive locations on a consignment basis beginning in February, 1954. The locations range from Long Island and Kure Beach on the Eastern Seaboard to San Francisco, San Diego and Seattle on the Pacific Ocean.

Out of 21 such experimental installations, only one unit required additional attention. This unit, at Narragansett, was blown from its location in 1954 during Hurricane Hazel and lay submerged in the ocean for two weeks. After removal from the ocean, the coating was found to be spotted with aluminum flashed from the conductors when the unit was uprooted. However, the finish was unaffected by this exposure.

Several capacitors coated with the system have been evaluated after 8400 hours in a 20 percent salt-fog. (ASTM B117-49T) At the end of the test, although terminals had corroded and some corrosion products had stained the surface of the capacitors, no penetration of the coating could be found. Under the same test conditions, an alternative standard dark grey finish might be expected to last 1400 hours.

Sandwich System Also Used

Transformer test covers have been coated with a sandwich system (primer, rubber base paint, dark grey finish) and exposed to the ASTM 20 percent salt-fog test for 6000 hours. At the end of the test, limited rusting had occurred at the sheared edges of the covers where

★ From a paper entitled "Melaprene—A Rubber Base Transformer Finish" by Ralph Hockridge, Distribution Transformer Dept., General Electric Co., Pittsfield, Mass.

Abstract

Salt fog and on-location test data are given for a resin-modified, chloroprene rubber finish used in paint systems applied to transformers. Data on transformers coated with the material indicate substantially improved service life in both atmospheric and subway or vault exposures. The material also exhibits improved resistance to some acids, alkalis, some hydrocarbons and distilled water in short-time, ambient temperature tests.

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paint coverage is difficult, but plane surfaces were unaffected.

Although salt-fog tests do not yield an absolute evaluation of materials, they can serve to distinguish between excellent, average and poor samples. Relative ratings, similar to those observed in salt-fog tests, have been noted in field trials at the G.E. Coastal test station on the shore of the Pacific Ocean at Oakland, California. In comparison to results achieved with salt-fog exposure, the rubber coating exhibits several times as much corrosion protection as a melamine modified alkyd and approximately 50 percent improvement over an oil modified phenolic formulation.

Two large network transformers for a submerged vault installation in Roanoke, Va., were finished with a Subway Black system. This consisted of one flowed coat of primer, two flowed, baked coats of Melaprene paint and two flowed baked coats of a phenolic base Subway Black. Average service before repainting in this location previously was six months. After one year the coating on these units was still in good condition, and they have been in service for more than 2½ years with no repainting necessary.

Chemical Resistance Excellent

The system offers excellent chemical resistance. Properly cured coatings have been exposed to various commonly encountered chemicals. Tests conducted at room temperature for 7 days are shown in Table 1. These data are offered mainly for comparison to a melamine modified alkyd.

The system presently applied to all G.E. transformers for underground service is as follows:

1. One coat of red-orange alkyd-melamine primer, flowed and oven-cured. This primer serves four main functions: a. Excellent adhesion to properly prepared steel, brass, copper and aluminum surfaces. b. Provides an excellent bonding surface for finish coats. Has high solids content to effectively fill blast profiles and contour irregularities. c. By means of corrosion inhibiting pigments such as iron oxide, zinc and basic lead chromates, it prevents serious corrosion of the metallic substrate should abrasion damage the finish.

2. Two coats of Melaprene, baked at high temperature. These coats can be flowed or sprayed. This intermediate rubber-base coating upgrades the finish by means of two primary functions: a. Gives a resilient backing for the finish coats, serving as an elastic cushion. Abrasion causes less damage because the coating "gives" under impact. b. Provides a secondary line of chemical defense to unusually severe corrosive conditions. This coating is preferred for intermediate use and not for finish coats because it develops a slight irridescence under prolonged exposure to sunlight. This discoloration, however, affects only the appearance, not the durability of the coating. Also, having a low gloss, somewhat matte appearance, spilled transformer oil and glove marks are noticeable.

3. Two coats of Subway Black, a 100 percent non heat-reactive (oil modified) phenolic. Each coat is oven cured. This finish is resistant to a wide variety of corrosive agents, including strong acids and weak alkalies. It is extremely water resistant and has a smooth, glossy surface not readily fingerprinted or oil stained. A further important function lies in its graphite pigmentation which equalizes and distributes stray electrical charges to reduce electrolytic pin-point corrosion which can proceed rapidly in wet or humid atmospheres, especially in the presence of salts.

4. An air-dry touch-up coating of a similar modified phenolic to cover minor abrasions occurring during assembly and final test. This coating gives a uniform appearance to the transformer.

Refinishing

Air drying forms of all materials are available for field refinishing. Shop refinishing is recommended; repainting is more satisfactory when done with proper cleaning and painting equipment.

TABLE 1—Resistance to Chemicals at Ambient Temperatures
(Seven days' test. Panels exposed to both chemical solution and chemical vapor pressure)

| Chemical	Rubber Coating	Alkyd-Melamine
Nitric acid 10%	Slight surface charring, Film unattacked	Blistering
Hydrochloric acid 10%	No attack	Film softening
Sodium hydroxide 10%	No attack	Complete removal
Ammonium hydroxide 10%	No attack	Blistering
Copper sulfate 10%	No attack	No attack
Kerosene	No attack	Slight softening
Ethyl alcohol	No attack	Loss of adhesion
Distilled water	No attack	No attack
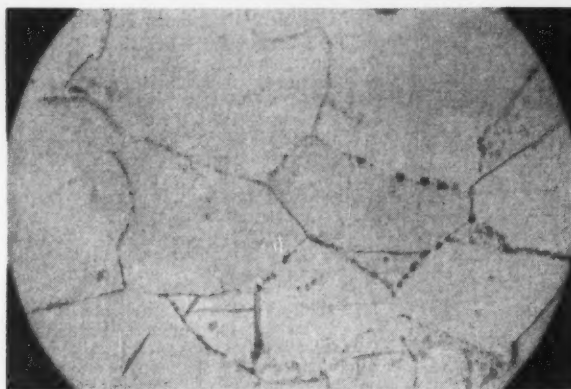
Figure 1—Surface of nickel showing intergranular graphitic embrittlement. Etchant was cyanide-persulfate. 500X.
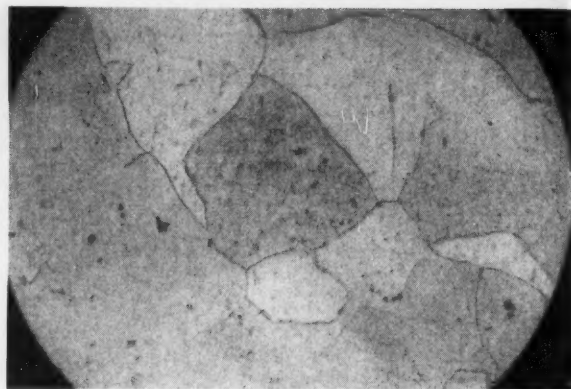

Figure 2—Surface of graphitically embrittled nickel after heat treatment. Etchant was cyanide-persulfate. 500X.

Recovery of Graphitically Embrittled Nickel*

NICKEL WAS selected as the material of construction for a shell and tube type heat exchanger for a high temperature process. Light gage tubes were welded to nickel tube sheets by the inert gas, tungsten arc method. After several days of operation, cracking occurred close to the welds. Change-over to schedule 40 nickel prolonged tube life, but failure occurred again. The tubes were badly embrittled over their entire length. Coke had accumulated on the interior surface of the tubes.

Examination

Analysis of the nickel revealed 0.10 percent total carbon, 0.06 percent graphitic carbon and 0.006 percent sulfur. Microscopic examination revealed the presence of considerable grain boundary precipitate which was optically anisotropic when viewed under plane polarized light. No evidence of sulfur attack was found.

Intergranular graphitic embrittlement of nickel can occur at about 455 C when carbon exceeds 0.03 percent. In this case graphite, occurring at the grain boundaries, had a pronounced detrimental effect on the ductility of the tubes with subsequent cracking caused by operating stresses. Figure 1 is a photomicrograph showing the etched surface of a nickel tube and the graphitic carbon in the grain boundaries.

Because coking occurred during process operation, low carbon nickel would not be suitable since it eventually would absorb enough carbon at the service temperature to become embrittled. Inconel, known to resist the environment, would not be susceptible to an embrittling phase such as graphite. Several Inconel tubes were installed on a trial basis. After several months of continuous service, no embrittlement could be detected. No failures have occurred after more than a year's service.

Heat Treatment

Because the nickel tubes remained in good condition, other than embrittle-

ment, a thermal treatment was attempted to restore ducility, thereby reclaiming the tubes for application in another process. Samples of severely embrittled nickel tubes were first cleaned and then given a 15-minute heat treatment at 1800 F followed by a water quench. Microscopic examination revealed some graphite still present in the grain boundries. Promise of successful recovery, however, was evidenced by the fact that the nickel tubes before this treatment could be broken easily with the fingers but afterwards could no longer be broken.

The nickel was given additional treatment at 1800 F for 30 minutes. Microscopic examination revealed that most of the embrittling phase had been redissolved or redistributed. Figure 2 shows the etched surface of a tube after heat treatment. No problems were experienced with welding or with threading of the thermally treated sections. A one-hour heat treatment at 1800 F followed by an alcohol-water quench was decided on as suitable for recovery.

Corrosion Resistance

Corrosion tests determined if loss in corrosion resistance had occurred as a result of the thermal treatment. The average test results on totally immersed coupons in sodium hydroxide and hydrochloric acid are shown in Table 1, comparing the resistance of thermally treated nickel with nickel which was not treated or embrittled. Little, if any,

Abstract

Heat treatment at 1800 F is discussed as a means of restoring almost full ductility to nickel tubing that had been graphitically embrittled. Corrosion tests indicate that the nickel that is heat treated can be used subsequently for other applications in which embrittling temperatures are not encountered. 3.7.3

decrease in resistance occurred in these environs.

Conclusion

The present limited data indicate that almost complete recovery of graphitically embrittled nickel can be achieved with the above thermal treatment and that nickel can be used subsequently for other applications where embrittling temperatures are not encountered.

Acknowledgment

The author acknowledges the International Nickel Company's evaluation of the embrittlement reported. Further acknowledgment is given to R. C. Talbot and R. N. Hobbs of the Hooker Chemical Corporation Corrosion Laboratory who assisted in the work.

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Exhibits at the 1959 Corrosion Show will be staffed by experienced corrosion engineers qualified to answer questions on corrosion control.

TABLE 1—Corrosion Resistance

NICKEL	Rate (average mils per year)	
	30% NaOH at 120 C* 3 Days	9% HCl at 105 C* 2 Days
Not treated or embrittled	0.30 ± 0.05	3.31 ± 0.08
Embrittled, treated 15 min. at 1800 F	0.38 ± 0.06	3.79 ± 0.07
Embrittled, treated additional 30 min. at 1800 F	0.39 ± 0.05	3.56 ± 0.12

* Approximate concentrations and temperatures.

CORROSION ABSTRACTS

1. GENERAL

1.2 Importance

1.2.2, 5.4.5, 8.5.3, 5.9.3

Capitalized Coating Costs Method Economical for Southeastern Pulp and Paper Mill Steel. HENRY T. RUDOLF. *Corrosion*, 13, No. 10, 129-130, 132 (1957) Oct.

A comparison is made between capitalizing coating costs for pulp and paper mills in the Southeastern part of the United States by sandblasting and precoating structural steel before erection with selected resin materials and the more common method of coating steel after erection and charging substantial recoating costs as a maintenance item. Savings in 10 years by using the capitalized cost method average $117,345 per 1000 tons after tax deductions.

A new standard of sandblasting is proposed which results in leaving adherent patches of scale not over 1-inch square and an over-all key pattern on the surface. **14244**

1.2.5, 6.3.15, 4.3.2

Explosions of Titanium and Fuming Nitric Acid Mixtures. L. L. GILBERT AND C. W. FUNK. *Metal Progress*, 70, No. 5, 93-96 (1956) Nov.

The effect of the concentration of fuming nitric acid on its shock-initiated pyrophoric reaction with commercially pure and iodide titanium sheet was investigated. The reaction was recorded by a cine camera and the equipment is described. Acid containing nitrogen peroxide > 6 and water $< 1.34\%$ is capable of initiating an explosion with titanium. The reaction is preceded by corrosion of titanium, but variations in alloy content, prior cold work, friction between two titanium surfaces and the presence of newly sheared edges did not affect the initiation of the explosion. Destruction of the passive oxide surface film followed by intergranular attack of the metal is probably the essential mechanism of the reaction.—MA. **13987**

1.6 Books

1.6

Engineering Materials Handbook. CHARLES L. MANTELL, Editor. Book, Jan., 1958, 1936 pp. McGraw-Hill Book Company, 327 W. 41st St., New York 36, New York.

In 43 sections devoted to metals, organic and inorganic materials and the cause and prevention of failure of materials, this book gives a comprehensive picture of the whole engineering materials field. Data covered include design information, structural characteristics, physical and mechanical properties, adaptations, advantages, limitations, competition with each other, protection against deterioration and other matters.

An 83-page alphabetical subject index enhances the value of the book. There are 35 references to corrosion. These relate principally to Section 37, Corrosion and Protection Against Corrosion prepared by T. P. May, The International Nickel Co., Inc., one of 150 contributors to the book. This section considers the theoretical aspects of corrosion, covers testing extensively, and examines the various factors that influence the corrosion rate of metals. Also covered are some aspects of inhibition by chemicals, concentration cells, and physical factors influencing corrosion, such as surface condition and stress.

Some attention is given also to protective coatings and the influence of design. Theoretical and practical aspects of cathodic protection are covered in some detail.

In the next section, 38, Materials of Construction for the Process industries, 18 pages of tabulated data are given on the corrosion resistance of materials to common process chemicals. These tables rate both metals and non-metallic materials. In Chapter 40, Gaskets, Packing and Seals, five pages of tabulated data are given on the resistance of gasket materials to corrosives. In Chapter 42, Materials Problems in the Petroleum Industry, considerable attention is paid to corrosion reactions of materials.

The volume of information in this book on corrosion and its prevention is extensive. **15162**

1.6, 2.4.3, 8.4.5

The Bettis Technical Review. Volume 1, No. 2. Reactor Metallurgy. Westinghouse Electric Corp. U. S. Atomic Energy Commission Pubn., WAPD-BT-2, July, 1957, 138 pp. Available from Office of Technical Services, Washington, D. C.

The Westinghouse physical metallurgy and nondestructive inspection programs are summarized. Discussions of and experimental results from studies of metal wear and friction in water, Bircaloy corrosion characteristics, order theory in AB_2 alloys, radiographic inspection and eddy current testing are presented.—NSA. **15146**

1.6, 3.7.2, 6.2.2

Boron, Calcium, Columbium, and Zirconium in Iron and Steel. FRANK T. SISCO, Editor. Book, 1957, 533 pp. John Wiley & Sons, 440 Fourth Ave., New York 16, New York.

This is the fourth volume of the new monograph series "Alloys of Iron Research" a publication project of the Engineering Foundation, New York. It correlates and summarizes data from hundreds of sources on the effects of the named metals as alloying elements in iron and steel. The accumulated information is valuable to corrosion workers concerned with high-temperature and high pressure applications of materials, especially in the rapidly expanding atomic and missile fields.

Authors R. A. Grange, F. J. Shortsleeve, W. O. Binder, D. C. Hilty and C. M. Offenhauer are known to corrosion workers directly or by reference. Numerous other experts contributed information and other services to complete the work.

The book considers the materials, effect on iron and steel in the order named

221a

in the title. Effect on structures, machining properties, heat treatment and other properties are reviewed. There is an alphabetical subject index and an alphabetical author index. 15091

1.6, 3.2.3, 3.5.9, 3.8.3, 5.9.4
Passivation Films and Coatings, Tarnish Coatings. H. FISCHER, K. HAUFFE AND W. WIEDERHOLT, Editors. Book, 1956, 400 pp. Published by Springer-Verlag, Reichpietschufer 20, Berlin W. 35, Germany.

This book is a collection of papers and discussions presented at the symposium on "Passivation and Tarnishing Phenomena" at Frankfurt-am-Main, October, 1955. There are 35 contributors, all, with one exception, from Germany. The aim of the symposium was "to present the current state of development in research and industry in such a way as to acquaint the practical man with the theories and methods of pure research on the one hand, and the theoretical scientists with the vast amount of experience accumulated in the applied field on the other."

Subjects such as the following have been discussed: high-temperature oxidation of metals and alloys in the thin-film and thick-film ranges; self-diffusion in oxides; mechanism of passivity; solubility of gases in metals; internal oxidation; Pourbaix diagrams; porosity of corrosion layers; atmospheric corrosion; anodizing; phosphating; electrolytic polishing. The subjects thus reach beyond the framework set by the title of the symposium. They may be divided into roughly two parts: the first (230 pages) dealing with the mechanism of oxidation phenomena, the second (160 pages) with problems of applied-corrosion work. The first part contains a fair amount of repetition, and most of the information may be found elsewhere, in current monographs for instance. The second part also is largely an account of published work, but it may contain a few hints of interest to the production scientists. The advantages and disadvantages of this type of book are well known. The advantage is that individual articles are written with authority by specialists in their fields; the main disadvantage is the lack of uniformity, this being particularly noticeable in the present volume.

A few minor points are: The solubility of oxygen in nickel is not unknown (p. 108); it was determined by Seybolt. The vacuum-fusion method is one for measuring gas contents and should not be classified under methods for the determination of equilibrium solubilities (p. 110); the "cold-extraction" is, I think no longer being used. The Pourbaix diagrams (e.g., p. 194) need a bit more explaining.

To sum up: The individual contributions are, on the whole, authoritatively written although the "concentration" varies, but the book suffers considerably from lack of editing. The relatively high cost, too, of the publication may exercise a restraining influence on many who would like to see it on their bookshelves. —MA. 13959

1.6, 3.1
Defects and Failures of Metals: Their Origin and Elimination. E. P. POLUSHKIN. Book, 1956, 399 pp. Elsevier Publishing Co., London.

A survey. Chapters on segregation, blowholes and porosity, pipes, impurities, decarburization of steel, scaling, residual stresses, fatigue, flakes, heat treatment, embrittlement, cracks, wear, corrosion. Each chapter has a bibliography. Most of the detailed discussion refers to iron and steel but reference is made to non-ferrous metals and much of the book is of general interest.—BNF. 13920

1.6, 3.1, 5.1, 4.1
Symposium on Corrosion Fundamentals. ANTON DE S. BRASUNAS AND E. E. STANSBURY, Editors. Book, 1956, 255 pp. Published by the University of Tennessee Press, Box 8540 University Station, Knoxville 16, Tennessee.

A series of lectures presented at the University of Tennessee Corrosion Conference at Knoxville on March 1, 2, 3, 1955. Includes: Corrosion and Metal Structures, E. E. Stansbury; Nature of Corrosion, A. de S. Brasunas; Atmospheric Corrosion, H. R. Copson; Coatings for Atmospheric Corrosion Protection, J. I. Richardson; High Temperature Corrosion, Henry Inouye; Liquid Metal Corrosion, E. E. Hoffman; Principles of Cathodic Protection, Milton Stern; Corrosion Problems in Steam Power and Industrial Boiler Plants, R. M. Lemen; Corrosion Failures in Chemical Plants, Mars G. Fontana; Inhibition of Metallic Corrosion in Aqueous Media, Harry C. Gatos; Passivation of Stainless Steel, N. A. Nielsen; The Influence of Mechanical Factors on Corrosion, J. J. Harwood; Geometric Factors in Electrical Measurements Relating to Corrosion and Its Prevention, W. J. Schwerdtfeger and I. A. Denison; Cathodic Protection Principles and System Design, H. C. Van Nouhuys; Use of Plastics and Plastic Liners for Corrosion Protection, R. B. Seymour. 13657

1.7 Organized Studies of Corrosion

1.7.1, 3.7.3
The 1955 Meeting of AEC Welding Committee, Savannah River Plant, September 7-8, 1955. Division of Reactor Development. U. S. Atomic Energy Commission Pubn., TID-7507 (Del.), July, 1956 (Declassified with Deletions Feb. 5, 1957), 248 pp. Available from Office of Technical Services, Washington, D. C.

The following reports were presented at the meeting of AEC Welding Committee; Welding of Type 347 Steels; Importance of Weld Composition and Hot Ductility with Respect to Austenitic Weld Cracking; An Evaluation of the Corrosion and Oxidation Resistance of High-Temperature Brazing Alloys;

Welding Problems Associated with the Construction and Operation of the MTR; Radiation Effects on Welds and Notches in Plain Carbon Steels, Stainless Steels and Nonferrous Alloys; and Some Nondestructive Testing Methods for Testing Welds.—NSA. 15225

1.7.1
Corrosion Convention. Papers before Corrosion Convention, London, Oct. 15-16, 1957. *Chem. & Process Eng.*, **38**, No. 11, 438-442 (1957) Nov.

Papers include: Protection of Plant and Equipment in the Petroleum and Chemical Industries by H. B. Footner; Selection of Corrosion-Resistant Metals and Alloys by J. B. Cotton; Vinyl Resins in the Construction of Chemical Plant by W. E. Martin; Metal and Plastics Coatings by G. H. Jenner, Anti-Corrosion Coatings for Buried Pipes by W. D. Parker and A. G. Wilkie; Corrosion in the Atomic Energy Industry by M. D. Jepson, D. White and L. Harbourne (discusses use of 18-8 titanium, 18-13 niobium steel and Zircalloy in atomic energy industry); Fuel Additives in the Fight Against Corrosion by B. J. Zaczek and R. Grindley; Paints and the Part they Play in the Fight Against Corrosion by H. Hollis and L. J. Coleman.—INCO. 15198

2. TESTING

2.3 Laboratory Methods and Tests

2.3.6, 3.2.2
Surface Finish Determination on Pitted Specimens. CHARLES W. DONNELLY. Knolls Atomic Power Lab. U. S. Atomic Energy Comm. Pubn., KAPL-M-AME-2, December 27, 1956, 11 pp. Available from Office of Technical Services, Washington, D. C.

Upon examination of test section elements, it was observed that there were two distinct types of surface finish present: Either a machined surface or a pitted surface. Standard profilometer measurements of the two surfaces showed no significant difference in value. A method was developed to measure the number of pits per square inch, the depth, diameter and distribution of the pits in the elements. The method consists of a modified Zyglo fluorescent dye penetrant technique combined with photo optical procedures. The method yields results which permit direct comparison of the elements tested. (auth).—NSA. 13573

2.3.7
Measurement of Adhesion of Paint Films. G. FUCHSLOCHER. *Deut. Farben-Z.*, **11**, No. 2, 63-64 (1957).

Ultrasonic and ultracentrifuge methods are considered to yield the best results but the much simpler impulse methods developed by the author are highly satisfactory.—RPI. 13740

2.3.7, 6.3.15
An Evaluation of Compression-Testing Techniques for Determining Elevated-Temperature Properties of Titanium Sheet. W. S. HYLER. Titanium Metallurgy Lab., Battelle Memorial Institute, June, 1956, 73 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121615). 13620

2.3.7
Brittle Fracture Initiation Tests. C. MYLONAS, D. C. DRUCKER AND L. ISBERG.

Paper before Am. Welding Soc., Nat'l. Fall Mtg., Cleveland, October 8-12, 1956. *Welding J.*, **36**, No. 1, 9s-17s (1957) Jan.

Laboratory tests generally fail to initiate brittle fracture at nominal stresses below yield except by extreme cooling or impact loading; literature is reviewed. Present investigation is study of conditions under which barrier to static initiation of brittle fracture is lowered. Welded and unwelded notched steel plates with various prestrains were pulled at various temperatures. Transversely prestrained plates with punched notches fractured consistently below yield under static loading. In two cases plates failed at little more than 70 percent of yield. Fractures showed no visible evidence of appreciable plastic deformation, and seemed to be of same type as encountered in catastrophic fail-

ure of storage tanks and ships. Stress-strain curves, tables, photographs of fracture specimens, 46 references.— INCO. 13797

3. CHARACTERISTIC CORROSION PHENOMENA

3.7 Metallurgical Effects

3.7.1, 2.3.7
Influence of Some Alloying Elements on the Susceptibility of Steel to Temper Embrittlement. M. L. BERNSHTEIN. *Metallovedenie i Obrabotka Metallov*, **2**, No. 9, 25-30 (1956).

Discussion of importance of estimating susceptibility of steel to temper brittleness on basis of impact tests run at several temperatures instead of only one to

find true brittle-to-ductile transition temperature. Effect of carbon, aluminum, boron and vanadium on a steel with 0.2 silicon, 0.6 manganese, 0.8 chromium and 1.4 nickel are given. Cause of temper brittleness is redistribution of elements during heat treatment, leading under certain heat treatment conditions to an unfavorable accumulation of elements in the intergranular zones. Redistribution of elements at grain boundaries is connected with adsorption of elements during heat treatment. Graphs, tables, 13 references.—INCO.   13967

3.7.1, 1.6

The **Foundations of Metallography**. G. MASING (Translated by F. C. Thompson). Inst. Metals Monograph and Report Series No. 21, 1956, 166 pp. The Institute of Metals, 4 Grosvenor Gardens, London SW 1, England.

Fundamental discussions on metallurgy include structure of alloys, process of crystallization, heat-treatment, recrystallization and corrosion and oxidation.—INCO.   13624

3.7.2, 3.5.9, 6.3.10

The **Relation Between the Chemical Composition, Temperature and Heat Resistance. III. Quintuple System of Nickel-Chromium-Tungsten-Aluminum-Titanium Alloy.** (In Russian.) I. I. KORNILOV AND F. M. TITOV. *Bull. Acad. Sci., URSS* (Izvest. Akad. Nauk, SSSR), Chem. Sci. Sec., No. 10, 117-122 (1956) Oct.

Composition and polythermal diagrams plotted for nickel-chromium-tungsten-aluminum-titanium alloys in a wide range of temperatures (up to 1250°) showed the complex relations between the heat resistance, chemical composition and temperature. Transitions from one temperature to another caused quantitative and qualitative changes in the composition-heat-resistance diagram. At lower temperatures (600 to 900°) the saturated solid solutions in the process of slow decomposition have a higher heat resistance than the homogeneous alloys. The maximum heat resistance (1000 to 1100°) was attained by alloy complexes in the transition from maximum saturation to supersaturation of the solid solution.—NSA.   13625

3.7.2, 3.8.4

Influence of Alloying Elements on Hydrogen Content and Hydrogen Mobility in Steel. YU. A. KLYACHKO AND T. S. IZMANOVA. *Stall,* **17**, No. 6, 507-511 (1957). Translation available from Henry Brutcher, Technical Translations, P. O. Box 157, Altadena, California.

Study of effect of titanium, silicon, carbon, manganese and zirconium on hydrogen content of as-cast and as-forged steel specimens and on rate of hydrogen effusion ('mobility') during holding at room temperature for various periods of time. Effect of size of specimens on liberation of hydrogen at low temperatures. Particulars on steel compositions studied. Distribution of hydrogen across the section of small ingots; influence of hot working on hydrogen content. Evaluation of results, six figures.—HB.   15321

3.7.2, 3.2.2, 6.2.3

The **Influence of Nickel on Susceptibility to Embrittlement During Long-time Creep-testing of Cast Chromium-Molybdenum and Chromium-Molybdenum-Vanadium Steel.** W. FELIX. *Arch. Eisenhuttenw.,* **28**, 710-712 (1957) Nov.

Report of 550 C creep tests on smooth and notched specimens of low-alloy cast

chromium-molybdenum and chromium-molybdenum-vanadium steels to assess the influence of up to 1.5 nickel on susceptibility to embrittlement.—INCO.   15263

3.7.2, 5.9.4, 6.4.2

Notes on the Anodic Oxidation of Aluminium Alloys Containing Copper. (In French.) JEAN HERENGUEL AND PIERRE LELONG. *Rev. Aluminium,* **34**, No. 249, 1197-1200 (1957) Dec.

Studying the effects of copper contents in aluminum on the anodizing process, the following observations have been made: (1) If the copper content is not entirely in a state of solid solution, the intermetallic compound Al_2Cu is formed which is violently attacked during electrolysis; (2) In the case of uniform and homogeneous solid solution the rate of oxide formation decreases in inverse proportion to the copper content; (3) The upper and lower limits of current density and temperature which are suitable for obtaining a continuous and sufficiently compact film are narrowed down very considerably; and, (4) Pieces containing copper and anodized by the sulfuric acid process often show brassy discolorations.—ALL.   15309

3.7.2

Molybdenum in Corrosion-Resistant Steels and Alloys. L. WETTERNIK. *Werkstoffe u. Korrosion,* **7**, No. 11, 628-633 (1956) Nov.

Review of applications of molybdenum in corrosion-resistant nickel-chromium and chromium steels and nickel-iron alloys. Data are given on dependence of corrosion-resistance in hydrochloric acid and sulfuric acid on molybdenum content of nickel-iron alloys containing 35, 28 and 60 nickel, nickel-copper-iron alloys, nickel-chromium and nickel-chromium-copper steels.—INCO. 13432

3.7.3

Self-Fluxing Airproof Brazing Alloys. N. BREDZS AND H. SCHWARTZBART. Paper before Am. Welding Soc., Nat'l. Spr. Mtg., Philadelphia, April 8-12, 1957. *Welding J.,* **36**, No. 7, 348s-352s (1957) July.

Self-fluxing, airproof brazing alloy can be made by adding another highly reducing element to lithium-bearing brazing alloy. Element must have same high affinity for oxygen at brazing temperatures as has lithium. Most important prerequisite is that binary phase diagram of both oxides must have at least one eutectic point with melting point considerably below solidus temperature of given brazing alloy. Combination lithium-boron is almost ideal. Lithium borates have excellent fluxing properties. Brazing experiments have shown correctness of foregoing approach. A 76 copper-18.3 nickel-4.75 lithium-0.75 boron alloy has been used to braze steels in air, without fluxes or protective atmospheres. Although not commercially feasible because of poor corrosion resistance and tendency for segregation in its preparation, this alloy demonstrates principles outlined. Both difficulties are due to complete insolubility of lithium in solid nickel or copper. Tables, phase diagram of LiO_2-B_2O_3 system.—INCO.   14711

3.7.3, 6.2.5

Time-Temperature Effect on Properties of Weld Heat-Affected Zone of Type 347 Stainless Steel. E. F. NIPPES, B. SCHAAF, W. L. FLEISCHMANN AND R. L. MEHAN. Paper before Am. Welding Soc., Nat'l. Spr. Mtg., Buffalo, May 9-11; Am. Soc. Mech. Engrs. Metals Eng. Div. Conf., Buffalo, May 7-11, 1956.

Welding J., **36**, No. 6, 265s-270s (1957) June.

Work presented is concentrated on behavior of samples heated in synthetic welding cycles (on RPI time-temperature controller) to peak temperature of 2450 F. Specimens were given various sensitization treatments. X-ray diffraction studies showed that in addition to CbC and/or CbN found in all samples, sensitization treatments produced $Cr_{23}C_6$ and sigma phase. To indicate importance of nickel content, tests were conducted on three different compositions of Type 347. Tests were also conducted on simulated specimens of Type 304 to establish base line for evaluation of Type 347 data. Results of room temperature and 1200 F Tensile tests, room temperature Charpy V-notch impact tests, and notched-bar stress-rupture tests at 1200 F showed that mechanical properties of Type 347 weld heat-affected zones are not impaired by high temperature treatments. Corrosion tests (65 percent boiling nitric acid test and Strauss acidified boiling cupric sulfate solution test) do indicate definite correlation between sensitizing treatments and corrosion rates. Corrosion rate initially increases with increasing times and temperatures, then decreases. Increasing sensitizing time and temperature leads to agglomeration of chromium carbide phase which was responsible for intergranular corrosion; free chromium diffuses into depleted regions at grain boundaries and decrease in corrosion rate is noted. Tables, graphs, photomicrographs.—INCO.   14721

3.7.3, 6.2.5

Welding Precipitation-Hardening Stainless Steels. G. E. LINNERT. 1956 Adams Lecture, Am. Welding Soc. *Welding J.,* **36**, No. 1, 9-27 (1957) Jan.

By selecting 3 particular grades of precipitation-hardening stainless steels 17-4 PH, 17-7 PH and 17-10 P as representative of single treatment martensitic steels, double treatment martensitic steels and austenitic steels, respectively and directing attention to metallurgical conditions encountered in welding these steels, information on welding practice of all grades of precipitation-hardening stainless steel is revealed. In considering welding of 17-4 PH, behavior in fusion welding, cracking in base-metal heat-affected zone, notch sensitivity and notch effect in design, notch circular-groove and maltese-cross weld tests and weld metal characteristics, are discussed. In welding 17-7 PH, 3 distinct structural conditions are created by the described hardening treatment, alternate hardening treatment for higher strength and treatment of cold-worked 17-7 PH. Due to strong ferrite-forming effect of aluminum, small amount of delta ferrite is always present in structure of 17-7 PH. Aluminum effect on surface of weld pool, weld metal cracking and porosity encountered in inert gas-metal and tungsten arc welding of 17-7 PH are considered. Resistance welding of 17-7 PH is reviewed. No successful method of fusion welding for 17-10 P has been devised to date; experience in resistance flash-butt welding, and arc and gas welding is discussed. Numerous photomicrographs.—INCO.   13468

3.7.3, 6.2.3

Changes in the Corrosion Resistance of Hardened Steel Due to Annealing. (In Ukrainian.) K. F. STARODUBOV AND S. G. CHERNIAVS'KA. Dopovidi Akademii Nauk, Ukrains'floi SSR (*Repts. of the*

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Academy of Sciences of the Ukrainian SSR), No. 2, 140-142 (1956).

Experimental data on variation of corrosion resistance of carbon steel with temperature of annealing. Corrosion curve shows two sharp maxima at about 275 and 400 C.—MR.   12620

3.7.3

The Effect of Carbon on Mechanical Properties, Corrosion Resistance and Structure of 25 Chromium-20 Nickel Weld Metal. K. WATANABE. Hitachi Hyoron, Special Issue No. 16, 6-12 (1956); *Library Abs. Bull.,* Japan, No. 3, VI-7 (1956) July-December.

25-20 weld metal has good corrosion and heat resistance but is subject to cracking. Influence of carbon was investigated. Carbon content has a close relationship with mechanical properties: toughness is improved with 0.07-0.14 carbon but columnar fracture develops with under 0.06 and 0.16-0.28 carbon. Carbon content has little influence on corrosion resistance of the weld metal to sulfuric acid, but in hydrofluoric acid + nitric acid or in the Strauss solution the corrosion of the weld metal is markedly enhanced as carbon increases. As carbon decreases, the non-metallic inclusions increase and the latter as well as the precipitated carbides may cause brittleness. —INCO.   13725

3.7.3

Basic Characteristics of Some Heat Resisting Brazing Filler Materials. W. H. CHANG. *Welding J.,* 35, No. 9, 431s-443s (1956) Sept..

Advantages and limitations of nickel-chromium-boron, nickel-chromium-silicon and gold-nickel brazing filler materials are evaluated on the basis of experimental results. Effect of surface preparation, brazing time, temperature and atmosphere, base-material integranular penetration and joint clearance on room temperature tensile properties of butt joints in 20 nickel/20 chromium/20 cobalt superalloy, 18/10 chromium/nickel steel and 12 chromium-steel brazed with these filler materials.—BNF.   13562

3.7.3, 6.4.2

Joining Aluminium to Other Metals. *Materials and Methods,* 45, No. 4, 200-204 (1957).

Four major factors must be considered; coefficient of expansion, heating cycle, heat conductivity and accelerated corrosion. In soldering steel to aluminum, clearances must permit the solder to run. Prolonged or slow heating impairs the efficiency of the fluxes. In composite assemblies heat should be applied to the largest part or to the best heat conductor. In cases where flux removal by washing is difficult a special soldering procedure is used.—MA.   15396

3.7.3

Symposium Surface Defects in Steel Products. *J. Australian Inst. Metals,* 1, No. 1, 1-48, 52 (1956) May.

Six papers: Surface Defects in Steel Products Attributable to Steelmaking, J. B. Kelly (pp. 1-6); Surface Defects in Steel Products Produced by Rolling-Mill Operations, E. J. Buckman (pp. 7-17); Defects in Steel Sheets, R. A. Parker (pp. 18-26); Surface Defects in Steel Tubing, R. S. Thomas (pp. 26-33); Steel for Drop Forging, H. J. Merchant (pp. 33-39); Surface Defects on Drawn Steel Wire, C. James (pp. 40-48, 52).— BNF.   13161

3.7.3, 6.4.2

The Properties of AlZnMgl Alloy Welds. ALBRECHT MULLER-BUSSE. *Z. Metallkunde,* 47, No. 7, 486-490 (1956).

The properties of the alloy AlZnMgl, which contains zinc 3.5-4.8, magnesium 0.5-1.2, manganese up to 1.0, chromium up to 0.3, copper <0.7, and iron <0.7%, are discussed. 2- and 8-mm-thick sheets of this material in the solution-treated, water-quenched and age-hardened condition were joined by gas or argon-arc (Sigma process) welding, using filler wires of similar alloy composition or AlSi5. The tensile and fatigue properties of the welded materials were determined after welding and after subsequent room-temperature ageing for 1 day and 1 and 3 months and compared with those of the original material and in the case of the fatigue tests, with similarly welded AlMg5. After gas and Sigma welding the original tensile properties are regained after ageing for 3 months at room temperature. The fatigue strength of AlZnMg1 decreases after welding, by 1/5 and 1/3 in the case of gas and Sigma welding, respectively, but is still considerably higher than that of welded AlMg5. The corrosion-resistance—to a solution containing 3% sodium chloride + 0.1% hydrogen peroxide and to the weather—of welded AlZnMg1 is good, and similar to that of welded AlMg5.— MA.   13693

3.7.3

Applications of Furnace Atmospheres —Bright Heat Treating the Non-Ferrous Alloys. C. E. PECK. Paper before Ind. Heating Equipment Assn.—Am. Soc. Metals Mtg., Oct. 9, 1956. *Metal Progress*, **71**, No. 3, 104-112 (1957) March; *ibid.*, **72**, No. 3, 70-75 (1957) Sept.

Prepared atmospheres are specified for bright annealing, bright hardening and for carburizing or carbo-nitriding of all varieties of plain, alloy and stainless steels and suggestions are given as to the atmospheres conventionally used, their dew points and C potentials. Atmospheres are specified for successful bright annealing of principal non-ferrous metals and alloys, including copper-nickel, copper-beryllium, nickel-iron, nickel-chromium and platinum, to avoid dezincification of brasses and to protect properly powder metal compacts during sintering, or combinations during furnace brazing. Tables, photos.—INCO.
14993

3.7.3

Bonding of Light Metals. J. J. MEYNIS DE PAULIN. *Rev. Gen. Mecan.* (N.S.), **41**, No. 100, 191-196 (1957).

A review of bonding processes and materials, with the design of joints. Hot- and cold-bonding media are tabulated with setting and hardening temperatures and conditions and strength of bonding of various adhesives. Corrosion effects and resistance to heat and moisture are noted.—MA.
15020

3.7.3

Multi-Purpose Heat Treat. E. A. SCHOEFER. Alloy Casting Inst. *Metal Progress*, **72**, No. 3, 83-87 (1957) Sept.

Description of 2 in-and-out batch-type carbo-nitriding furnaces, a washing machine and unique arrangements of roller conveyers for hardening small parts made of various types of steel and cast iron. Because components are exposed to a wide variety of high temperatures and gas atmospheres Type HT cast alloy is used for all grids and associated fixtures, as well as parts for the furnace hearth. Type HT (35 nickel, 15 chromium, 50 iron) was selected because it has excellent hot strength at operating temperatures and good life under rapidly fluctuating temperatures. Summary of industrial experience on corrosion resistance of alloy to various environments is given. Photos, graphs, tables.—INCO.
15080

3.7.3, 8.8.1

Corrosion of Weld Joints. (In German.) H. ZITTER. *Schweisstechnik*, **10**, No. 9, 113-117 (1956) Sept.

Examples of corrosion of various types of steel in the chemical industry. Experimental data. Methods of minimizing corrosion.—BTR.
13736

3.7.3, 6.2.5

A Note on the Furnace Cracking of an Austenitic Stainless Steel. F. A. HODIERNE. *J. Iron Steel Inst.*, **185**, Pt. 2, 225-227 (1957) February.

Cold-drawn tubes of 18-10 stainless containing niobium cracked transversely on heating for interpass softening. Cracking was reproduced experimentally at 650-950 C and appears to be associated with precipitation of intergranular carbides with high internal stress. Cracking is avoided by precipitating carbides at 850 C before cold-drawing tubes. Table, photomicrograph.—INCO.
13772

3.7.3

Properties of Austenitic Chromium-Manganese Stainless-Steel Weld Metal. W. T. DeLONG AND H. F. REID, JR. Paper before Am. Welding Soc., Nat'l. Fall Mtg., Cleveland, Oct. 8-12, 1956. *Welding J.*, **36**, No. 1, 41s-48s (1957) Jan.

Study covers properties of chromium-manganese stainless steel weld metal as determined by tensile, impact, bend and crack tests and work-hardening and plastic deformation evaluation. Alloys covered composition range: 0.10-0.90 carbon, 7-18 manganese, 0-21 chromium and 0-4 nickel. Effects of varying chromium, nickel, manganese and carbon contents and of other alloy additions (niobium, tungsten, molybdenum, cobalt, vanadium) on strength and ductility of 16-1-16 were determined and properties compared with conventional Type 308, 310, 312 and 347 weld metals. Promising 16-1-16 alloys combine very high strength with reasonable ductility and high crack resistance in restrained joint with completely nonmagnetic structure. Potential applications are listed. Tables, graphs, photomicrographs.—INCO.
13769

3.7.3, 6.2.5

The Importance of Weld Composition and Hot Ductility with Respect to Austenitic Weld Cracking. O. R. CARPENTER AND R. D. WYLIE. Paper before U. S. Atomic Energy Comm., Welding Committee, Sept. 8, 1955. *Metal Progress*, **70**, No. 5, 65-73 (1956) Nov.

Difficulties occurring in welded stainless steel equipment in high-temperature service led to new composition which is free from weld cracks and is superior to Type 347 electrode in all respects except resistance to intergranular corrosion. Croloy 16-8-2 chromium-nickel-molybdenum composition equals or betters all mechanical properties of Type 347, as shown in results of Navy Dept. Bureau of Ships study of weldability of 18-8 molybdenum steels in which new weld material was developed. Work covered studies of 25 different base materials of 18-8 and 18-8 molybdenum analyses and 18 different weld metal compositions. Results are given for following: weld deposit soundness, mechanical properties of weld and base materials, service properties (Charpy V notch impact after ageing for 10,000 hr.) and effects of weld restraint on properties. Tables, photographs.—INCO. 13539

3.7.4

The Characteristics of the Bond Interface Formed Between Zircaloy 2 and Uranium-12 w/o Molybdenum. HENRY A. SALLER, STAN J. PAPROCKI AND EDWIN S. HODGE. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-1048, Oct. 17, 1955 (Declassified Feb. 26, 1957), 50 pp. Available from Office of Technical Services, Washington, D. C.

The interface formed between a uranium-12 w/o molybdenum core alloy and Zircaloy 2 was investigated to determine its structure and corrosion behavior in high-temperature water. Assembled picture-frame-type elements were pressure bonded under conditions which yielded various degrees of interdiffusion. The bonded specimens were defected through the Zircaloy 2 cladding into the alloy core with a 40-mil hole and corrosion tested in 650 F water. Those bonds which possessed a minimum amount of diffusion were most corrosion resistant. The corrosion resistance decreased progressively with increased

interdiffusion. Specimens with extensive bond diffusion failed by rupturing at the interface in less than 1 hr. of exposure in 650 F water. The various alloy layers of the interface were identified and individual alloys were prepared and evaluated in high-temperature water. The alloy layers which exhibited poor corrosion resistance in the interface also possessed poor resistance when tested as discrete alloys. The least-resistant alloys were those possessing 12 w/o molybdenum with small amounts of zirconium replacing the uranium of the base core alloy. Transition layers between the uranium-12 w/o molybdenum core alloy and Zircaloy 2 were investigated in an effort to obtain a more resistant interface than was obtained by direct bonding. Of the layers that were investigated, chromium, platinum and tantalum were the best, but none of these layers was sufficiently effective to warrant further study. An exploratory study to determine the effect of different barrier layers on the interdiffusion of Zircaloy 2 and uranium-3.8 w/o silicon alloy was also made. (auth.)—NSA. 15074

3.7.4, 6.4.2

Influence of Crystallographic Orientation on the Corrosion Rate of Aluminum in Acids and Alkalies. T. H. OREM. *J. Research National Bureau of Standards*, **58**, No. 3, 157-167 (1957) March.

Corrosion of single crystals of high-purity aluminum in strong acid and alkali media is disclosed as an orderly process, rate of attack being dependent on orientation of corroding surface. For a 15% sodium hydroxide solution, corrosion progressed by revealing facet surfaces of the (335) type, resulting in gross corrosion of spheres into cubes; in contrast, corrosion in aqua regia-hydrofluoric acid mixture revealed etch pits with surfaces of the (100) type, resulting in gross corrosion of spheres into equilateral octahedra. Photomicrographs, diagrams, 15 references.—INCO. 13926

3.7.4

Intercrystalline Corrosion and Attack at Grain Boundaries. F. ERDMANN-JESNITZER. *Werkstoffe u. Korrosion*, **9**, No. 1, 7-16; disc. 16 (1958) Jan.

Dependence of intercrystalline corrosion on degree of disorientation of contiguous grains was investigated in an aluminum-7 magnesium alloy which was rendered susceptible to intercrystalline corrosion by heat treatments. Experiments show that intercrystalline attack is very much dependent upon the degree of disorientation with points of attack at 4 and 16 degrees. Explanation of results in terms of lattice energy and lattice geometry leads to distinction of fine, micro and micro angle grain boundaries. Author finally shows that intercrystalline attack is caused by inhomogeneous separations of one or more phases at grain boundaries of more than 5 degrees but not by the elastic potential lattice energy. Graphs, photomicrographs.—INCO. 15171

3.8 Miscellaneous Principles

3.8.2, 6.4.4, 3.4.9

On the Rate-Determining Step of the Hydrated-Water Reaction in Corrosion of Magnesium in Aqueous Solutions of Neutral Salt. (In Japanese.) GORO WADA. *J. Electrochem. Soc., Japan*, **25**, No. 4, 164-165 (1957) April.

When magnesium is corroded in the aqueous solutions of neutral salts, under

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the catalytic action of their ions, the process is expressed as follows:

$$(Mg)_s + 2H_2O \rightarrow (Mg)_s \cdot 2H^+ + 2OH^- \quad (1)$$

$$(Mg)_s \cdot 2H^+ \rightarrow Mg^{2+} + H_2 \quad (2)$$
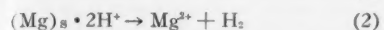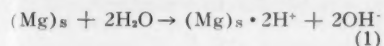
where the water molecules denoted in Eq. (1) mean those which are hydrated to ions in the solution.

On the other hand, the reaction by the local cells formed by the combination of magnesium with metals which are nobler than magnesium, is expressed as follows:

Anode: $Mg \rightarrow Mg^{2+} + 2e^-$ (3)

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (4)
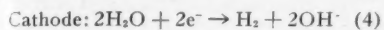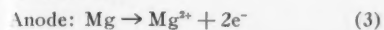
In this paper, the volumes of the evolved hydrogen at both electrodes were measured, when magnesium as anode and platinum as cathode were dipped in 1 N solution of potassium chloride and were connected by wire with each other under various working voltages in order to examine the relation between the hydrated-water reaction and the electrode reaction. Since the volume of hydrogen at platinum was equivalent with the value from the coulometer and the volume of hydrogen at magnesium was independent of the latter, it was concluded that the evolution of hydrogen at magnesium is caused from the hydrated-water reactions (1) and (2) and the evolution of hydrogen at platinum is attributed to the electrode reaction (4).

The experimental results on the rate of the electrode reaction v_{Pt}, the rate of the hydrated-water reaction v_{Mg} and their ratio $\alpha = v_{Pt}/v_{Mg}$ at various temperatures and terminal voltages are listed.—JSPS.
14395

3.8.2, 6.3.21, 4.7
Electrochemical Behavior of Bismuth. Diagrams of Equilibrium Tension-pH of System Bismuth-Water at 25 C. (In French.) J. VAN MUYLDER AND M. POURBAIX. Centre Belge d'Etude de la Corrosion, Rapport Technique No. 48, May, 1957, 13 pp. Available from CEBELCOR, 21 rue des Drapiers, Brussels, Belgium. 14388

3.8.3, 6.2.2, 5.9.4
Investigation of the Anodic Passivation of Iron in Dilute Acid Solution. Part I. (In Croatian.) B. LOVRECEK AND K. BOSNJAK-MOSLAVA. *Zastita Materijala*, 5, 9-11 (1957) Jan. 13818

3.8.3, 6.4.2, 3.6.5
The Static Electrode Potential Behavior of Aluminum and the Anodic Behavior of the Pure Metal and Its Alloys in Chloride Media. E. M. KHAIRY AND M. KAMAL HUSSEIN. *Corrosion*, 13, No. 12, 793t-798t (1957) Dec.

The electrode potential behavior of aluminum investigated in buffer solutions of pH 4-8 containing varying concentrations of chloride ions, shows that the electrode potential does not respond to variations of pH. It changes linearly with pCl yielding a more or less constant E'_0 value of —0.54 volt. The corroding effect of the chloride ions supposedly is restricted to the adsorption of these ions on the surface and the electrode behaves as one of the second type.
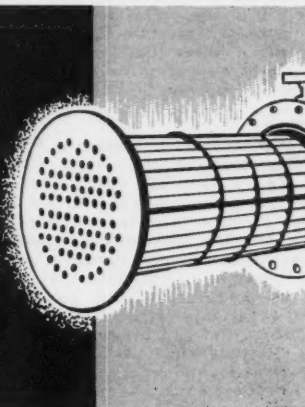
The oscillograms obtained both with the pure metal and with its alloys indicate that the surface oxide resists the corrosive effect up to a 0.1-N [Cl⁻]. At higher concentrations, the electrode surface is appreciably activated acquiring relatively high double layer capacities, prominent passivity being achieved only on passing appropriate amounts of electricity. 14503

3.8.3, 6.3.6
Anodic Behavior of Metals. Pt. IV. Copper in Sodium Hydroxide Solutions. (In Polish.) ZDZISLAW ZEMBURA. *Roczniki Chem.*, 31, No. 2, 627-635 (1957).

An attempt to elucidate the mechanism of passivation of copper in sodium hydroxide solutions, based chiefly on the analysis of the curves of the ratio

between the anodic current density and the anode potential during voltage controlled electrolysis. 9 references.—MR.
14794

3.8.3, 6.3.19, 2.3.5
On the Periodic Variations in Current Intensities During the Anodic Dissolution of Zinc. Pt. 1. (In German.) K. SCHWABE. *Metalloberflache*, **11**, No. 1, 1-6 (1957) Jan.

After stating some theoretical considerations regarding the passivity of surface layers, a table giving anodic reactions is discussed. This is followed by the description of the method used for investigating the anodic dissolution of zinc in unsaturated solutions of its salts. Periodic variations in current intensities were observed with some salts as soon as saturation was reached at the anode. The variations differ according to the anion or salt mixture used. There are upper and lower limits of current densities and temperatures where no variations are observed.—ZDA. 14787

3.8.2
Fundamentals of Electrode Processes in Corrosion. MILTON STERN. *Corrosion*, **13**, No. 11, 775t-782t (1957) Nov.

Recent advances in the theory of electrode kinetics provide a simple means for explaining many of the experimental observations made in the corrosion field. The concepts of exchange current, activation polarization, and concentration polarization are introduced in an effort to bridge the gap between the work of the electrode kineticist and the practicing corrosion engineer. Many of the early classic experiments in the field of corrosion are discussed along with modern observations of the effects on corrosion rate of solution velocity, galvanic coupling, and metal environment composition. 14435

3.8.2, 6.3.21
Electrochemical Behavior of Arsenic. Equilibrium Diagram of pH vs. Tension of the Arsenic-Water System at 25° C. (In French.) J. VAN MUYLDER AND M. POURBAIX. Centre Belge d'Etude de la Corrosion, Rapport Technique No. 46, Feb., 1957, 1-14. Available from CEBELCOR, 21 rue des Drapiers, Brussels, Belgium.

On the basis of free standard enthalpy values of the various constituents, a diagram of this system was established as a function of the pH and of the electrode voltage at 25 C. Passivating action of the arsenical compound on iron and ordinary steels in acid solution was determined.—BTR. 14352

3.8.2, 6.4.2, 4.3.3
Contribution to the Study of the Corrosion of Aluminium in Alkaline Media. HELMY MAKRAM. *Comp. Rend.*, **244**, No. 26, 3153-3154 (1957) June 24.

Copper plates covered with aluminum foil of commercial purity were subjected to an electrolytic process, where the electrolyte consisted of sodium hydroxide solutions of different concentrations. It was observed that in all cases the potential of the plate, compared to a reference element, varied as a function of time and gradually approached a constant value which corresponded to the potential of the base metal. The point where the potential-curve reaches a plateau represents the end of the corrosion process of aluminum. From the time-component of this evolution the corrosive power of the electrolyte is evaluated.—ALL. 14719

3.8.2, 5.8.3
Surface Corrosion Rule and Effect of Inhibitors on Electrochemical Corrosion. (In German.) H. E. HOMIG. *Werkstoffe u. Korrosion*, **8**, 321-324 (1957) June.

This rule is valid under certain conditions only. These conditions can be derived from the fundamental rules of corrosion processes mathematically so that one can obtain a general law of which the classical surface rule is a special case. For anodic and cathodic controlled corrosion processes the surface rule is perfectly valid at certain ratios of the cathodic to the anodic areas, and only approximate valid at other ratios Assuming a simplified mechanism for certain inhibitors it is possible to determine the effects of adding inhibitors from the general surface law.—MR. 14695

3.8.2, 6.3.8
Measurement of Electrode Potential and Observation of Surface States by the Use of Radioactive Tracer. (In Japanese with English Summary.) MASAO MAEDA. *J. Electrochem. Soc., Japan*, **25**, No. 4, 195-199 (1957) April.

The behavior of the lead anode in solution containing sulfate ions is characterized by the complexity of the electrode processes due to the formation of two successive layers, i.e., lead sulfate and lead dioxide layers.

The present experiments were conducted in order to obtain some fundamental information concerning corrosion and protection of lead.

Experimental procedures and results are given.

Conclusions: a) Change of anodic potential with the lapse of time shows three arrests, each of which corresponds to the well known electrode process. b) It is suggested that the rate determining process of formation of lead oxide from lead sulfate film is initially nucleous formation of lead oxide, next the outward diffusion of SO_4^{2-} or other ions through the pores or grain boundaries of PbO_2-film. c) After the anode surface is completely covered with lead oxide, the formation of lead oxide stops and oxygen gas evolves from the surface because of its electron conductive property.—JSPS. 14422

3.8.2
Electrochemical Behavior of Boron. Diagrams of Equilibrium-Tension-pH of the System Boron-Water at 25 C. (In French.) E. DELTOMBE, N. DE ZOUBOV AND M. POURBAIX. Centre Belge d'Etude de la Corrosion, Rapport Technique No. 47, March, 1957, 19 pp. Available from CEBELCOR, 21 Rue des Drapiers, Brussels, Belgium. 14402

3.8.2, 6.3.6, 4.3.2
Anodic Transients of Copper in Hydrochloric Acid. RALPH S. COOPER. *J. Electrochem. Soc.*, **103**, No. 6, 307-315 (1956) June.

Anodic transients for the system copper hydrochloric acid were studied using horizontal anodes shielded to prevent convection. With the exception of the appearance of a second plateau the results are in quantitative agreement with Muller's Bedeckungstheorie. The reaction occurring during the first plateau is $Cu + Cl^- \rightarrow CuCl + e^-$. The second plateau is due to the initiation of a new reaction involving the OH^- ion. Potential measurements and visual observation indicate it to be $2Cu + 2OH^- \rightarrow Cu_2O +$

$H_2O + 2e^-$. Studies made with 0.5-6N hydrochloric acid show the layer thickness to be given by a relationship of the form $\delta = Di_1^{-m}$ with m independent of concentration and $D \propto$ concentration. These results were compared with some obtained with vertical unshielded anodes to determine the effect of convection. For rapid transients (<3 sec.) Muller's theory held with both types of anode. Otherwise results were qualitatively similar with the exception of the appearance of overshoot and a steady state with the unshielded anodes. 13 references.—MA.
13555

3.8.2
The Electrochemical Basis of Corrosion. (In French.) J. BRENET. *Corrosion et Anti-Corrosion*, **4**, No. 9/10, 317-329 (1956) Oct., Nov.

A study of current opinions about corrosion as a phenomenon produced by electrochemical reactions.—BTR. 13538

3.8.2
The Mechanism of Metal Corrosion Under Thin Layers of Electrolytes. (In Russian.) I. L. ROSENFEL'D AND T. I. PAVLUTSKAYA. *Zhur. Fiz. Khim.*, **31**, 328-339 (1957) Feb.

The corrosion current of elements in thin layers of electrolyte (70 to 165μ) is determined by the rate of the cathode process. The over-all corrosion current in thin layers is less than during complete immersion of the element in the solution but the current density at the site of contact of the electrodes is higher for films than bulk solutions.—BTR.
15034

3.8.2
Lessons on Electrochemical Corrosion. Pt. III. (In French.) M. POURBAIX. Centre Belge d'Etude de la Corrosion, Rapport Technique, No. 49, July, 1957, 68 pp.

Electrochemical equilibria. Oxidation and reduction. Galvanic cells. Electrochemical reactions. Equilibrium diagrams of water with copper, silver, lead, tin, iron, zinc, aluminum and arsenic.—BTR.
14990

3.8.2
Some Aspects and Problems of the Electrochemistry of Metals Encountered in a Decade of Study and Research. R. PIONTELLI. *Metallurgia Italiana*, **49**, No. 2, 69-88 (1957).

Piontelli discusses: General theory and definitions; theory of and experimental results on overvoltage; metal displacement reactions; the influence of anions on electrochemical kinetics; the influence of the structure of metallic materials on their electrochemical behavior; throwing power; the distribution of current between various electrochemical reactions; electrochemical models; definition and interpretation of the phenomena of passivation and the condition of passivity; processes of electrolytic polishing; the electrochemistry of alloys; the electrochemistry of fused salts; practical applications of the results with regard to the improvement of existing processes and the development of new ones, with particular reference to the use of sulfamate electrolytes in the refining of lead, the anodic oxidation of aluminum and the electrodeposition of nickel. 139 references.—MA. 14997

3.8.3
Internal Electric Potential Drop in the Passive Layer of Iron and the Flade

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Potential. (In German.) H. GOHR AND E. LANGE. *Naturwissenschaften*, **43**, No. 1, 12-13 (1956).   13988

3.8.3, 5.9.2, 5.9.4

Corrosion Study. V. Mechanism of Chemical Passivation and Corrosion of Metals. (In German.) M. PRAZAK AND V. PRAZAK. *Coll. Czech. Chem. Communs.*, **21**, No. 3, 564-570 (1956) June.

Comparison of chemical and electro-chemical passivations and corrosion of iron in nitric acid of various concentrations.—MR.   14010

3.8.3, 6.2.5

The Activation and Passivation of Stainless Steel in Aerated Sulfuric Acid. G. H. CARTLEDGE. *J. Electrochem. Soc.* **104**, No. 7, 420-426 (1957) July.

Potential-time curves have been determined at 85 C for a niobium-stabilized stainless steel during its transition to the state that is essentially stable in aerated 0.1 N sulfuric acid. Experiments were conducted both with pre-oxidized specimens and with others that were previously saturated with hydrogen by electrolysis. It was found that the potential passes through characteristic inflections and an attempt was made to relate these to the processes with which they are associated. In particular, it was found that, for the conditions used, there is a "critical recovery potential" above which spontaneous passivation occurs and this potential was shown to be approximately equal to the hydrogen potential for the same conditions. The corrosion rate was shown to be characteristically related to the changes in potential.   14245

3.8.3, 6.2.5

Recent Observations on the Passivity of Stainless Steel. M. G. FONTANA AND W. P. MCKINNELL, JR. *Werkstoffe u. Korrosion*, **8**, 249-254 (1957) May.

Review of recent literature on two theories of passivity in metals (formation of an oxide skin; adsorption of an oxide film), with reference to iron and to 18/8-type stainless steels which are passive in oxidizing solutions. Data and theories on passivity mechanism in 18/8 and results of work at Ohio University on adsorption of oxygen at surface of Type 304 stainless steel at room temperature are given. Results tend to corroborate oxide film theory.—INCO.   14294

3.8.3, 6.3.10

Effect of Temperature on the Passivity of Nickel. (In Japanese with English summary.) GO OKAMOTO, HARUO KOBAYASHI, NORIO SATO AND MASAICHI NAGAYAMA. *J. Electrochem. Soc., Japan*, **25**, No. 4, 199-203 (1957) April.

An investigation was carried out to determine the effect of temperature on the passivity of nickel to bring light on the intrinsic nature of its passive film. Many investigators have suggested the existence of the protective oxide-film on the surface of the passivated nickel. However, the nature and behavior of this passive film are still beyond complete understanding. Since no detailed report on the electrochemical behavior of nickel has been published, the anodic polarization characteristics and the electrode impedance of the passivated nickel was determined in 1 N sulfuric acid at a temperature range of 30～95 C. Experimental procedure is given.

Results are: (1) Anodic polarization curves of nickel obtained in 1 N sulfuric acid at 39 C and 71 C are given. Passivation occurred above the critical potential of about $+0.3$ V. The passive state was stable in a potential range from $+0.45$ V

to $+0.65$ V and the anodic current κ was found constant in this region. (2) It was observed that the passive nickel corroded very slowly with the constant corrosion rate which was independent of the potential. Assuming that the passive nickel dissolves into solution as Ni^{++}, this corrosion rate was found to be equivalent to κ at both temperatures. (3) Frequency characteristics of the impedance of the passive nickel which was stable at $+0.55$ V in a range from 0.2 to 20 KC are given. Similar types of frequency characteristics have been reported on the passive iron in chromate solution and on undeteriorated painted steel in sodium chloride solution. (4) The temperature dependency of κ is shown. A discontinuous change and a hysteresis phenomenon were observed at about 60 C in the log $\kappa \sim 1/T$ relation. The apparent activation energy above and below this critical temperature were 21.1 ± 0.0 Kcal/mol and 18.8 ± 0.0 Kcal/mol, respectively. (5) The temperature dependency of tan δ of the passive nickel at the frequency of 1 KC is shown. The value of tan δ changes very little in the region below 60 C while it increases steeply with increasing temperature above 60 C.—JSPS.   14179

3.8.3, 5.9.4, 6.4.2

Nature of the Passivation Film on Aluminum from a Study of the Behaviour of an Electrode of This Metal and from Anodic Polarization. A. RIAD TOURKY, E. M. KHAIRY AND M. KAMAL HUSSEIN. *J. chim. phys.*, **53**, 433-439 (1956); *Chem. Absts.*, **50**, No. 18, 12696-12697 (1956) Sept. 25.

Examination of the behavior of an aluminum electrode which was initially free of Al+++ ions gave a curve E /pH resembling the solubility curve of aluminum hydroxide over an extended region of pH (pH 5 to pH 8) and in which the electrode behaved like a metalmetallic oxide electrode subject to an excess pressure of oxygen. At below pH 4 and above pH 8 the oxide formed by pre-immersion dissolved; the potential corresponded respectively, to the systems Al/Al+++ and Al/AlO₂⁻ and became subject to the effect of an excess pressure of hydrogen. The experiments on anodic polarization by the method of periodic oscillography on the same series of coupons gave the same order as far as the formation of the film and its stability were concerned. The unpacked coupons containing solutions of the ions SO₄⁻, NO₃⁻, or Cl⁻ gave a stability for the film producing passivation which was not only the function of the activity of the H⁺ ion present but which was also sensibly influenced by the anions in the order $SO_4^- < NO_3^- < Cl^-$. The authors showed that a stable oxide in the presence of NO₃ and Cl ions was formed by a second process of hydrolysis. On similar films oxygen was evolved in the vicinity of its reversible potential (1v). Films producing stable passivation in the presence of SO₄⁻ ions and in coupons were characterized by an oxide film from which oxygen was evolved at potentials much above 2.5v.—ALL.
13390

3.8.3, 6.2.2

On the Nature of the Passive Film on Iron in Acid Solutions. (In Russian.) A. M. SUKHOTIN. Uspekhi Khimii (Progress in Chem.), **25**, No. 3, 312-328 (1956).

A review of recent, primarily German, publications on the mechanism of origination, retention and destruction of passive films on iron. Properties of the passive film and problems of activation and passivation of iron in acid solutions are discussed. Graphs, table. 45 references.—BTR.
12641

3.8.4, 8.4.5

Oxidation Behavior of Reactor Materials. R. A. U. HUDDLE. First Nuclear Engineering and Science Congress, 1, 79-89 (1957).

Attempt to develop a theory of oxidation involving principles of crystal chemistry as opposed to electronic considerations which can be applied as a basis of alloying to improve oxidation resistance. Relation to oxidation behavior of nuclear fuels, canning materials, structural metals. 15 references.—MR.
14886

3.8.4, 6.3.20, 4.6.2, 3.4.6

The Oxidation of Zirconium and Its Relationship to Corrosion in High Temperature Water. D. E. THOMAS AND J. CHIRIGOS. Westinghouse Electric Corp. U. S. Atomic Energy Commission Pubn., WAPD-98, October 15, 1953 (Declassified March 9, 1957), 25 pp. Available from Office of Technical Services, Washington, D. C.

The kinetics of oxidation of alpha zirconium in dry oxygen were determined and found to differ from the kinetics of corrosion in high-temperature water. The data suggest that the mechanism of reaction with the two media is similar except that an additional factor operates in water corrosion whose effect is not pronounced until the more or less protracted initial low corrosion rate is supplanted by a higher corrosion rate. (auth.)—NSA.
15106

3.8.4, 6.2.2, 3.5.9

Contribution to the Study of Oxidation of Iron in Air Between 700 and 1250 C. (In French.) JEAN PAIDASSI. *Revue de Metallurgie*, **54**, 569-585 (1957) Aug.

Studies on Armco iron and "Puron" indicate that the skin is formed by three continuous and compact ferric oxide, Fe₅O₄ and ferrous oxide layers, the isothermic growth rate of which is parabolic. The relative thicknesses of the layers in relation to total thickness remain practically constant and are respectively 1, 4 and 95% of the total.—BTR.
15008

3.8.4, 3.7.4

The Epitaxial Growth and Oxidation of Nickel, Cobalt, and Iron on Rocksalt. L. E. COLLINS AND O. S. HEAVENS. *Proc. Phys. Soc.*, (B), **70**, No. 3, 265-281 (1957).

Electron-diffraction examination of the structure and orientation of nickel, cobalt and iron deposited by thermal evaporation on rocksalt and their oxides, formed spontaneously on the epitaxially grown metal films, show that the lattice misfit between substrate and deposit material is generally less important than the maintenance of correct co-ordination of atoms in the first layer. Generally no evidence of a strained deposit lattice was obtained except for ferrous oxide films on iron.—MA.
14932

3.8.4, 3.4.8, 3.8.3, 6.3.20

Adsorption and Incorporation of Sulfuric Acid Anions in Zirconium Oxide Films. (In Italian.) M. MARAGHINI AND M. SERRA. *Ricerca Scientifica*, **27**, 2468-2474 (1957) Aug.

Passivity of zirconium surfaces obtained through oxidation (by air or anodic action) is destroyed by chlorine ions in the presence of SO₄ ions at a certain concentration ratio. By tagging sulfate ions with radioactive S³⁵ it was demonstrated that the destruction of the passivity coincides with a process of replacement of chlorine ions by SO₄ ions within the protective film. 12 references. —MR.
15018

6. MATERIALS OF CONSTRUCTION

6.2 Ferrous Metals and Alloys

6.2.1, 8.1.2

Corrosion of Metals in Buildings. J. C. HUDSON AND F. WORMWELL. *Chemistry and Industry,* **76**, No. 32, 1077-1089 (1957) Aug. 10.

A large number of cases of corrosion of ferrous metals are discussed and corrective measures proposed. 12 references.—MR.
14674

6.2.4, 6.2.5, 3.5.9

Development of Heat-Resistant Materials and Their Testing in Czechoslovakia. J. PLUHAR. *Arch Eisenhuttenw.*, **28**, 707-710 (1957) Nov.

General review of Czech progress in evolution of heat-resistant ferritic and austenitic materials for elevated-temperature service, particularly in power plants. Creep strengths and corrosion behavior of ferritic steels and iron-base alloys are given. Materials tested include low-alloy chromium-vanadium, chromiummolybdenum-vanadium, chromium-tungsten, chromium-molybdenum-tungsten steels, 13/12/1.25 titanium-stabilized chromium-nickel-tungsten steel and highalloy manganese-chromium-titanium and manganese-chromium-vanadium steel.

Test methods to supplement creep data are given.—INCO.
15014

6.2.4, 8.4.5

Low-Cost Materials for Sodium Heat Transfer Systems. E. G. BRUSH AND R. F. KOENIG. Knolls Atomic Power Lab. Chemical Eng. Progress Symposium Series, *Liquid Metals Technology*—Part 1, **53**, No. 20, 59-65 (1957).

Ferritic alloy steels have several advantages which make them attractive substitutes for austenitic stainless steels in sodium cooled nuclear power plants where temperatures do not normally exceed 1000 F. However, a major question attending their use in sodium is their resistance to corrosive attack. Although to date no sodium cooled power-producing unit has made widespread use of the low-alloy steels, laboratory tests indicate that these steels possess satisfactory resistance in sodium to mass transfer, to attack by oxygen, to decarburization and to diffusion bonding at temperatures up to 1000 F. Photomicrographs, graphs, tables, 13 references.—INCO.
15189

6.2.4, 3.7.4, 3.5.9

An Investigation of Three Ferritic Steels for High-Temperature Application. A. P. COLDEN AND J. W. FREEMAN. University of Michigan. U. S. Wright Air Development Center, U. S. Air Force. April, 1957, 117 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 131069).

Relationships were examined between microstructure and high-temperature properties at 700 to 1100 F of a nickelchromium-molybdenum steel and two chromium-molybdenum-vanadium steels. The results correlate properties with microstructure for three temperatures of isothermal transformation in the pearlite region and three in the bainite region. Optimum structures (and treatments) were shown to vary with both the alloy and test conditions. In general, bainitic structures gave best properties. However, for the chromium-molybdenum-vanadium steels, pearlites formed at relatively low temperatures were often as strong or stronger than the baintes. Tempered martensite was never the strongest structure and most often was the weakest.—OTS.
15187

6.2.5, 4.3.2

Corrosion of Type 347 Stainless Steel by 1st Cycle Raffinate. A. R. OLSEN. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-51-10-31, October 4, 1951 (Declassified Feb. 20, 1957), 4 pp. Available from Office of Technical Services, Washington, D. C.

A boiling corrosive medium of pH 1.3 consisting of 2.2 M aluminum nitrate, mercuric nitrate-5 wt % of aluminum as murcury and 0.79 M NH₄ (added as ammonium hydroxide to produce 0.2 normal acid deficiency) was used for these tests. Tabular data are presented. —NSA.
15012

6.2.5, 7.2

Analysis of Types of Corrosion Encountered in 18/8 Stainless Steel Tubing: Causes and Prevention. (In French.) J. DEDIEU AND L. PENNEC. *Corrosion et Anticorrosion*, **5**, No. 11, 348-358 (1957) November.

Discussion of corrosion failures in 18/8, 18/8 molybdenum and 18/8 CuMo tubing, including failure due to intergranular and stress-corrosion, fissuring and weld decay. Notes on methods of prevention and control, including prior heat-treatment are given.—INCO. 15215

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6.2.5, 6.2.2

British and American Standard Steels. W. B. KEMMISH. *Materials in Design Eng.*, **46**, No. 5, 6; 171, 173, 175, 177; 167, 169, 171 (1957) Oct., Nov.

Comparison in tabular form of SAE steels and En series steels giving composition, heat treatment temperature (carburizing, hardening and tempering), quench medium and mechanical properties (tensile strength, elongation and hardness). Data are listed for free machining and carbon steels, low carbon steels for cold forming operations, manganese, manganese-molybdenum, nickel, nickel-chromium, nickel-molybdenum, nickel-chromium-molybdenum, manganese-nickel-chromium, chromium, chromium-molybdenum, spring, corrosion and heat resisting steels.—INCO. 15331

6.3 Non-ferrous Metals and Alloys—Heavy

6.3.15, 4.3.2

Corrosion of Titanium. D. W. STOUGH, F. W. FINK AND R. S. PEOPLES. *Light Metal Age*, **15**, 20-22 (1957) Feb.

Titanium corrosion resistance is good in general and is especially valuable in environments of sea water, nitric acid, chromic and acetic acid, ferric and cupric chlorides. It is possible to inhibit the attack of hydrochloric acid, sulfuric acid, oxalic acid and formic acid but the attack of hydrofluoric acid cannot be inhibited. Galvanic attack of the other metal in a galvanic couple is a problem. Titanium is subject to crevice corrosion in some acid environments; reactions with corrosive environments are often complex. There is a tendency to polarize the galvanic current between titanium and other metals.—MR. 15061

6.3.15, 4.3.6, 3.5.8, 3.5.9

Progress Report on the Salt Corrosion of Titanium Alloys at Elevated Temperature and Stress. Titanium Metallurgical Laboratory. Battelle Memorial Institute. Nov., 1957. 57 pages. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121637).

A type of high-temperature corrosion of titanium alloys by sodium chloride is described which, in the presence of stress, may lead to cracking. Four titanium producers and an aircraft company carried out an extensive research program to determine the time, temperature and stress levels at which this reaction occurs. This report contains results of their study in terms of limiting conditions for stress corrosion in commercial alloys, preventive measures against elevated temperature stress corrosion and the mechanism by which the stress corrosion occurs.—OTS. 15188

6.3.15, 3.7.3

Principles and Application of Heat Treatment for Titanium Alloys. A. J. GRIEST AND P. D. FROST. Titanium Metallurgical Lab. Battelle Memorial Inst., December, 1957, 132 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121636).

The state of the art of titanium heat treatment is summarized as of Spring 1957. A section describes relationships between alloy constitution, microstructure and properties obtained on heat treatment. Another contains a collection of property data for selected commercial alloys in the heat-treated condition. Room-temperature and short-time-elevated temperature data are presented for all of the alloys. A third section discusses heat-treating practice, including furnace characteristics, coatings for minimizing contamination and procedures for the control of distortion and flatness during heat treatment.—OTS. 15278

6.3.17

Aqueous Corrosion of Uranium and Alloys: Survey of Project Literature. J. W. McWHIRTER AND J. E. DRALEY. Argonne National Lab. U. S. Atomic Energy Commission Pubn., ANL-4862, May 14, 1952 (Declassified February 7, 1957), 49 pp. Available from Office of Technical Services, Washington, D. C.

The corrosion rate of uranium in hydrogen-saturated and air-saturated water is reported. The effects of dissolved gas, hydrogen peroxide, dissolved salts, velocity, surface preparation and heat-treatment on aqueous corrosion of uranium are discussed. Aqueous corrosion of niobium-uranium, molybdenum-uranium, silicon-uranium, uranium-zirconium and aluminum-uranium alloys was studied and the effect of alloying constituents on corrosion rate is reported. (auth.)—NSA. 14986

6.3.17, 4.6.2, 3.4.6, 3.7.2

Corrosion of Uranium-Zirconium Alloys in Water at Temperatures up to 100 C. H. A. PRAY AND W. E. BERRY. Battelle Memorial Inst. U. S. Atomic Energy Commission Pubn., BMI-893, December 16, 1953 (Declassified February 26, 1957), Available from Office of Technical Services, Washington, D. C.

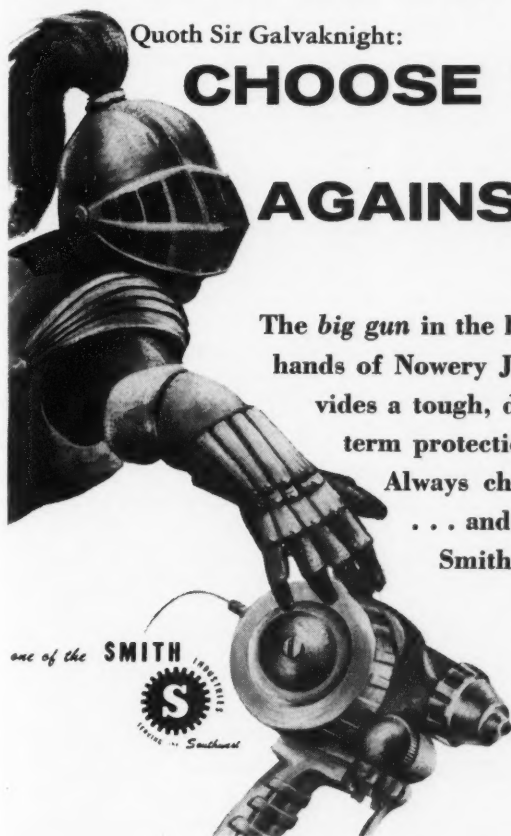Under certain conditions, uranium-5 wt% zirconium alloys exhibit remark-

able corrosion resistance in distilled water at 100 C after 1-year's exposure. The alloy must be quenched rapidly (in water or oil) from above 700 C. Subsequent treatments to soften it by annealing at 500 or 600 C or by isothermal treatments have lessened its resistance. Corrosion resistance is also dependent on dissolved oxygen in the test water. The alloy is resistant to 97 C water saturated with hydrogen-oxygen mixtures in ratios up to 25 to 1 but not in excess of 35 to 1. It corrodes when part of a crevice. Harmful effects of surface abrasion can be removed by a nitric acid pickle and long-time pickling does not impair corrosion resistance. Galvanic coupling uranium-5 wt% zirconium with aluminum does not adversely affect the corrosion resistance of the alloy. Increasing the zirconium content to about 7.5 wt% eliminates the alloy's sensitivity to crevice effects and to dissolved oxygen in the test water, while additions in the range of 20 wt% eliminate the need for special heat treatments. (auth).—NSA. 15053

6.3.17, 4.6.2

Resume of Uranium Alloy Data—VI. B. LUSTMAN. Westinghouse Electric Corp. U. S. Atomic Energy Commission Pubn., WAPD-MM-491, Jan. 3, 1955 (Declassified Feb. 1, 1957), 54 pp. Available from Office of Technical Services, Washington, D. C.

Data are summarized on the corrosion of uranium-molybdenum alloy in 343 C water, the corrosion of uranium-molybdenum-platinum alloys in 650 F water, the corrosion life of unclad uranium-molybdenum-niobium alloys in 650 F water, the corrosion behavior of uranium-molybdenum-X alloys in 650 F water, the corrosion life of zircaloy-clad uranium alloys, dimensional changes in irradiated uranium-silicon alloy specimens and hardness changes in uranium-molybdenum alloys during corrosion testing. Macroscopic observations of uranium dioxide powders and compacts are also shown.—NSA. 14969

6.3.6

Copper and Copper Alloys: A Survey of Technical Progress During 1956. E. VOCE. *Metallurgia*, 55, No. 329, 109-120 (1957).

A review of developments in production, founding, fabrication, finishing and plating, joining, inspection and analysis. Progress in physical and powder metallurgy, corrosion, properties of alloys and industrial applications are considered. 276 references.—MA. 15134

8. INDUSTRIES

8.1 Group 1

8.1.4, 4.6.6

On the Causes of Internal Corrosion and Clogging in Water Mains. (In Italian.) R. SANDRINELLI. *Ingegneria Sanitaria*, 5, 48-51 (1957) March-April.

Problem of corrosion of steel mains for potable water, with special reference to formation of nodular incrustations which, in addition to inducing corrosion, cause stoppage and reduction in carrying capacity; formation of heavy mineral incrustations not connected with corrosion but which contribute to obstruction of piping.—MR. 15078

8.1.1, 8.6.3

Controlling Corrosion of Textile Mill Air Conditioning Equipment. J. STANLEY

LIVINGSTONE. *Corrosion*, 13, No. 11, 147-148 (1957) Nov.

Operating conditions of air conditioning equipment in textile mills are described. Some design defects are pointed out and remedial measures suggested. A procedure related to available plant shut-down time for surface preparation and coating of central air conditioning systems is described in detail, together with some recommended coating systems. Vinyls and zinc rich paints are suggested as the best coatings available now for the application conditions prevailing. A paper presented under the title "Control of Corrosion in Air Conditioning Equipment in Textile Mills" at a meeting of Southeast Region, National Association of Corrosion Engineers, Atlanta, Georgia, May 3, 1956. 14425

8.4 Group 4

8.4.5, 6.4.2

Metallurgical Examination of H-Loop Fuel Elements Resulting from Rupture Incident. G. R. MALLETT. Hanford Atomic Products Operations, U. S. Atomic Energy Commission Pubn., HW-43557, August 13, 1956 (Declassified March 13, 1957), 16 pp. Available from Office of Technical Services, Washington, D. C.

The first and third slugs downstream from ruptured slug and a piece of the can wall from the ruptured slug were examined and the extent and type of aluminum corrosion were determined. It was found that the ruptured slug and the third one became severely warped. The ruptured one acted as a water heater causing inter-granular corrosion and excessive heat generation. The over-heated water caused aluminum intergranular corrosion. The indications are that the higher the water coolant temperature the less warp can be tolerated.—NSA. 15387

8.4.5

HRT-CP: Results of Solids Dissolution Tests. W. L. ALBRECHT. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-57-7-113, July 30, 1957, 6 pp. Available from Office of Technical Services, Washington, D. C.

A dissolution cycle in the chemical plant consists of refluxing with 10.8 M sulfuric acid for four hours followed by refluxing for a like period with 4 M acid. In each of three tests in which 370-gram batches of simulated corrosion product solids were subjected to two dissolution cycles using 820% excess acid, more than 99.6% of the solid material was dissolved (based on the amount of undissolved material collected). In another test, using one dissolution cycle and 820% excess acid, 99.5% of the solids material was dissolved. In the final test in which a 530-gram batch of solids was subjected to two dissolution cycles using 540% excess acid, only 91.7% of the solid material was dissolved. The corrosion rate of a specimen of Carpenter 20 suspended in the vapor space of the dissolver during these tests was 0.01 mil per year. (auth)—NSA. 14913

8.4.5, 6.4.2

Corrosion Problems in the NPR. R. L. LOFTNESS AND M. H. FELDMAN. North American Aviation, Inc. U. S. Atomic Energy Commission Pubn., NAA-SR-94 (Del.), 1951 (Declassified with Deletions February 27, 1957), 38 pp. Avail-

able from Office of Technical Services, Washington, D. C.

General concepts of corrosion and the available data on aluminum and stainless steel corrosion by water are summarized. Study of the aluminum-water system includes consideration of several alloy types, and of the influence of water temperature, flow rate, pH and dissolved material. The wide variance in reported values allows only tentative interpolation in a considerable region of possible operating temperatures. At 135 C, the corrosion rate of Type 2S aluminum is estimated at a maximum of 1.0 mil/month in the process water proposed, with the range 0.01 to 0.5 mil/month representing probable mean values. Possible ways of minimizing corrosion, such as anodizing and the use of inhibitors are discussed. Corrosion of stainless steel is shown to be negligible. The effect of corrosion and film formation on heat transfer is briefly considered. (auth).—NSA. 15355

8.4.5

Neutron Producer (CP-6) Program Technical Progress Letter; January 1952. STUART MCLAIN, Comp. Argonne National Lab. U. S. Atomic Energy Commission Pubn., ANL-4757, Feb. 12, 1952 (Declassified Feb. 12, 1957), 35 pp. Available from Office of Technical Services, Washington, D. C.

Rapid uranium oxidation in water was studied in a pressurized section of a loop containing a slug and heated internally by a calrod unit. The loop section if shown as well as the exposed section of the slug after oxidation and corrosion. Simultaneously with the loop tests, uranyl oxide solubility tests were also explored and reported. The decomposition of heavy water in the CP-3 has been measured for a helium gas flow of 7 cfm. The corrosion test results are tabulated for aluminum and aluminum-silicon specimens. Preliminary and first-phase tests of both the hydraulically operated bundle-type control rod and the hydraulically operated safety rod are reported. Out-of-roundness and low warping measurement of α-canned uranium slugs are reported. Analytical results are tabulated for the hourly values of uranium losses in the aqueous waste steam of box extractor. The results of a differential distillation of 800 ml of synthetic IAW solution spiked with radioactive zirconium are tabulated and graphed.—NSA. 15353

8.4.5, 6.2.5

Corrosion Problems in the Production of Nuclear Power. A. B. MCINTOSH. Paper before Soc. Chem. Ind., Chem. Ind., Corrosion Group, Jan. 9, 1957. *Chemistry and Industry*, No. 6, 166-167 (1957) Feb. 9; *Corrosion Prevention and Control*, 4, No. 3, 40, 92 (1957) March.

Maintenance is possible in chemical plants for extraction of uranium, but not in plants where plutonium is extracted. Development of chromium-nickel austenitic steels for constructional materials was considered. Co-operative effort resulted in adoption of 18 chromium-13 nickel stabilized by 1 niobium which was not lost during welding. 18-13-1 niobium corrodes at less than half the rate of 18-8-titanium in 70% w/w nitric acid at boiling point such as used in plutonium separation process. Effects of various influences on corrosion of stainless steels and welds, inhibition of accelerated corrosion by reducing agents (nitrogen dioxide) and mechanism of corrosion of stainless steel

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in boiling nitric acid were discussed. Further problems considered included corrosion of magnesium alloy cans (used to store fuel elements under water during cooling), corrosion in water at high temperature of stainless and mild steels, zirconium, aluminum and their alloys. In discussion T. P. Hoar questioned reference to stress corrosion cracking of stainless steel in steam containing no trace of chloride.—INCO.   15338

8.4.5

Aqueous Uranium Slurry Studies. J. O. BLOMEKE. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-1904, October 20, 1955 (Declassified January 17, 1957), 65 pp. Available from Office of Technical Services, Washington, D. C.

The possible use of aqueous uranium oxide slurries as reactor fuels has been investigated. It was found that U^{6+} was the most stable valence state in such slurry fuels. Several methods for the preparation of $U_2O \cdot H_2O$ are described. The crystal structure of $UO_2 \cdot H_2O$ was examined. Slurries of $UO_3 \cdot H_2O$ were tested for thermal stability, radiation stability, and corrosive properties.—NSA.   15194

8.4.5

Dounreay—Britain's Fast Reactor Project. H. E. B. ANDERSON. *Power Eng.*, 61, No. 11, 58-62 (1957) Nov.; *Can. Chem. Processing*, 41, No. 11, 70-72, 74-76 (1957) Nov.

Description of Dounreay Establishment. Fuel elements of fast breeder consist of enriched uranium rods, sheathed in niobium. Niobium is used to contain core elements because it has a high melting point and good resistance to hot uranium and sodium. Stainless steel is used for canning blanket elements since conditions in blanket are less severe than in core. Reactor core and breeder blanket are housed in a stainless steel reactor vessel. Secondary liquid metal coolant passes out of reactor sphere through stainless steel pipes to heat exchanger house. Use of liquid metal circuits and liquid-metal to liquid-metal heat exchangers for fast breeder reactor has necessitated special fabrication techniques in stainless steel in order to meet all conditions required. Highly active liquor wastes are stored in stainless steel tanks within heavily reinforced concrete underground vaults. Photos, diagrams.—INCO.   15197

8.4.5, 3.4.6

HRT Oxygen Addition System. F. C. ZAPP. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-56-3-42 and Add., March 2, 1956 (Declassified March 14, 1957). Addendum: March 21, 1956, 10 pp. Available from Office of Technical Services, Washington, D. C.

The addition of oxygen to the inlet or low pressure side of the Homogeneous Reactor Test fuel pumps is considered; oxygen addition at low reactor power levels is known to prevent uranyl ion reduction within the fuel solution and to prevent excessive corrosion of the stainless steel system. Details of addition system components and operating procedures are included.—NSA.   15181

8.4.5

The Homogeneous Aqueous Reactor. Part II. I. WELLS AND D. NEWBY. *Nuclear Eng.*, 2, 275-285 (1957) July.

The problems which are encountered in homogeneous aqueous reactors are considered, namely, corrosion, handling of slurries, safety, maintenance, methods of fabrication and gas production and its removal. A typical 2-zone system designed to produce 100 Mw of electricity is described. Reactors with burners and single zone reactors are described with particular reference to the systems of Foster Wheeler and Westinghouse. A list of homogeneous reactors proposed or under construction is given.—NSA.   15143

8.4.5

Power Plant Coolant Technology Program. S. L. WILLIAMS. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-M-SMS-74, July 5, 1957, 17 pp. Available from Office of Technical Services, Washington, D. C.

Brief summaries of studies of high temperature water purification; corrosion product distribution and activity buildup; coolant sampling techniques; high pH effects; coolant deaeration, chemical treatment, and radiation catalyzed reactions; and fission product contamination and removal are given.—NSA.   15152

8.4.5

The Heavy Water-Slurry Pile. H. C. UREY. Columbia Univ., New York. U. S. Atomic Energy Commission Pubn., A-743, June 30, 1943 (Declassified Feb. 14, 1957), 104 pp. Available from Office of Technical Services, Washington, D. C.

A brief evaluation is made of the slurry pile including the tube construction, the slurry properties, the product removal, shielding, and construction materials. Complete data are included on the stability of uranium oxide systems, the preparation and properties of slurries and corrosion and erosion of construction materials.—NSA.   15122

8.4.5

HRP Radiation Corrosion Studies: In-Pile Loop L-4-8. J. E. BAKER, N. C. BRADLEY, G. H. JENKS, A. R. OLSEN, H. C. SAVAGE AND F. J. WALTER. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-2042, August 21, 1956 (Declassified Jan. 17, 1957), 35 pp. Available from Office of Technical Services, Washington, D. C.

A fifth in-pile loop experiment, L-4-8, was completed. The loop operated in-pile for a total of 1637 hours during which time the LITR energy output was 4377 Mwhr. The average fission power in the loop based on cesium analyses was 622 w when the LITR was at full power (3 Mw). Based on oxygen data, the generalized corrosion rate for the first 300 hours was 4.0 mpy; the rate for the remaining 1337 hours was 0.7 mpy. The nickel data gave parallel results. The corrosion of the Type 347 stainless steel, Zircaloy-2, and titanium-55AX coupons exposed in the core and in in-line holders was generally consistent with that observed in previous in-pile loop experiments. Some differences with steel were attributed to the fact that this was the first loop containing steel specimens operated with $0.04m$ sulfuric acid present in the uranyl sulfate charge solution ($0.17m$ uranyl sulfate, $0.03m$ copper sulfate). Stress specimens, made from the alloys Zircaloy-2, Type 17-4 PH stainless steel, and titanium-carbon-130-AM, were exposed in core, in-line, and pressurizer locations. Microscopic examination and average weight loss gave no indication of effects attributable to the stressed condition of the specimens. (auth.)—NSA.   14921

8.4.5, 6.2.5

Reactions Between LMFR Fuel and Its Container Materials. Metallurgy Memo No. 586. W. E. MILLER AND J. R. WEEKS. Brookhaven National Lab. U. S. Atomic Energy Commission Pubn., BNL-2913, May 4, 1956 (Declassified April 12, 1957), 34 pp. Available from Office of Technical Services, Washington, D. C.

The most practical container materials from the corrosion resistance, mechanical properties and heat transfer considerations are the steels. Experiments were performed to study the problem of carbide formation by uranium and/or fission products in the bismuth reacting with the graphite moderator in a thermal reactor. Since zirconium has little effect on the rate of solution of iron in bismuth and an appreciable effect on the rate of solution of iron from steels, experiments were run to determine the nature of the surface deposit formed on the steels. Results from these experiments are described.—NSA   15375

8.4.5, 6.3.11, 4.3.3

Corrosion of Platinum by UO_2SO_4 Solutions Under Irradiation. G. H. JENKS. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-56-8-188, August 30, 1956 (Declassified March 19, 1957), 4 pp. Available from Office of Technical Services, Washington, D. C.

Results indicate that corrosion of the metal is accelerated to a small extent during irradiation. A summary of the results from in-pile loops and in-pile autoclaves is given.—NSA.   15327

8.4.5, 4.6.2

Corrosion Problems in Atomic Reactors Caused by Water at High Temperatures (Above 100 C). Pt. II Corrosion Reaction of Materials for Fuel Elements and Their Protective Envelopes. Pt. III. Corrosion Properties of Construction Materials Used for Building Reactors. (In German.) Willibald Machu. *Atomkernenergie*, 2, 248-255 (1957) July.

Corrosion of aluminum, zirconium and their alloys used as protective envelopes for uranium and thorium; stainless, heat-resistant and austenitic steels, chromium, nickel, cobalt, titanium, gold, platinum, silver, magnesium, copper and silicon carbide used as construction materials.—BTR.   15360

8.4.5, 6.4.2

Corrosion of an Aluminum-Nickel Alloy in a Reactor Test Loop. EMIL LOUIS MARTINEC. Argonne National Lab. U. S. Atomic Energy Commission Pubn., ANL-5783, Sept., 1957, 18 pp. Available from Office of Technical Services, Washington, D. C.

The results of the corrosion study are illustrated in a plot of the weight loss of the aluminum-nickel samples with respect to the time at test temperatures of 470 to 485 F. The corrosion rate determined by this test indicates that the weight loss per unit time is the same for both the in-pile irradiated specimens and the out-of-pile control specimens which did not have any neutron exposure, except that the out-of-pile specimens had a higher initial rate of corrosion which elevated the curve above that of the in-pile specimens. (auth.)—NSA.   15369

8.4.5

The Effect of Cyclotron Irradiation on the Physical Properties of Metals. A. B. MARTIN, M. TARPINIAN AND R. R.

EGGLESTON. North American Aviation, Inc. U. S. Atomic Energy Commission Pubn., NAA-SR-75 (Del.), Jan. 8, 1951 (Declassified with Deletions Feb. 27, 1957), 43 pp. Available from Office of Technical Services, Washington, D. C.

Metals and alloys were irradiated at about −150 C with a 33 Mev α beam. Electric resistivity, hardness, dimensions and lattice parameters were measured on aluminum, copper, zirconium, aluminum-uranium alloys, zirconium-uranium alloys, AuCu and AuCu₃ super-lattice alloys and a beryllium-copper precipitation hardening alloy before and after irradiation.—NSA.   15370

8.4.5
Proposed in-Pile Loop Experiment. G. H. JENKS, D. T. JONES, J. N. BAIRD AND J. L. REDFORD. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-54-3-196, March 31, 1954 (Declassified April 1, 1957), 35 pp. Available from Office of Technical Services, Washington, D. C.

A test system was devised for the study of radiation effects on corrosion in a homogeneous reactor system. Basically, the system consists of a small loop through which fuel solutions are circulated by a small centrifugal pump. Discussions are given on loop operating characteristics and design, insertion and removal procedures, and hazards.—NSA.   15316

8.4.5
HRP-CP: Analytical Requirements for the HRT Chemical Processing Plant. WILLIAM L. CARTER. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-56-4-101, April 9, 1956 (Declassified March 18, 1957), 11 pp. Available from Office of Technical Services, Washington 25, D. C.

The proposed analytical requirements for the Homogeneous Reactor Test chemical processing plant are tabulated for both infrequent and routine analyses conducted for determining fission product, corrosion product, off-gas, and fuel component concentrations in fuel and blanket systems.—NSA.   15186

8.4.5, 3.5.4
Interim Report on Effects of Reactor Radiations on Metals. Joint Report of Metallurgy and Physics Divisions. D. S. BILLINGTON. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-138 (Del.), October 27, 1948 (Declassified with Deletions March 6, 1957), 30 pp. Available from Office of Technical Services, Washington, D. C.

Reactor radiation effects on the physical properties of stainless steel, monel metal, nickel, steel, beryllium-copper alloys and various other alloys are summarized. Metallographic techniques for examining miscrostructures of irradiated samples are discussed.—NSA.   15192

8.4.5
Chemistry of the Ninth PWR Fuel Material Test X-1 Loop NRX Reactor. Interim Report covering period from start-up, January 18 to April 8, 1957. R. EHRENREICH. Westinghouse Electric Corp. U. S. Atomic Energy Commission Pubn., WAPD-CDA-(1)-3, 37 pp. Available from Office of Technical Services, Washington, D. C.

The ninth PWR Fuel Material test in the X-1 loop of the NRX reactor is a long term proof test for Zircaloy-2 clad UO₂ fuel specimens under irradiation at PWR reference conditions. One

of the fuel specimens was fabricated with a cladding defect. The test is scheduled to run for a period of one year and achieve a fuel burn up of 10,000 Mwd/ton of UO₂. Radiochemical analyses have been performed on loop water, purification resins and loop piping. The results up to and including the reactor shutdown after 80 days are presented. The progress of the test has been satisfactory to date with the exception of short periods of abnormally low levels of radionuclide activity. The fission product activity in the coolant during these low levels is what would be expected from uranium contamination. Consequently, it appears that the defect becomes plugged in some manner. (auth)—NSA.   15241

8.4.5, 4.7
Corrosion and Other Factors in the Application of Sodium to the KAPL Reactor. L. F. EPSTEIN AND C. E. WEBER. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-M-LFE-4, December 15, 1948 (Declassified March 25, 1957), 38 pp. Available from Office of Technical Services, Washington, D. C.

Data accumulated on the nature of the engineering and technological problems involved in the use of liquid sodium as a heat transfer medium in a nuclear reactor are presented. Some possible solutions are included.—NSA.   15246

8.4.5
Demonstrating Commercial Atomic Power—Process Flowsheet. T. P. FORBATH. *Chem. Eng.,* **64,** No. 8, 230-233 (1957) August.

Description of Argonne National Laboratory's experimental boiling water reactor. Steam from core is coupled directly to turbine, sidestepping intermediate exchangers. Water drains continuously from reactor through ion-exchange water-purification system. Mixed cation and anion resin beds remove hydrogen and oxygen ions produced by irradiation of water and disposable cotton filters remove corrosive and erosive particles. Diagram, photographs.—INCO. 15270

8.4.5, 3.4.3
Poisoning of the Core of the Two-Region Homogeneous Thermal Breeder. Study No. 1. A. T. GRESKY AND E. D. ARNOLD. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., CF-53-12-165, Dec. 11, 1953 (Declassified March 12, 1957), 30 pp. Available from Office of Technical Services, Washington, D. C.

An evaluation was made of the magnitude and nature of fission and corrosion product poisoning of the core solution in the Two-Region Homogeneous Thermal Breeder. A reasonable yield curve for U²³³ fissioning has been established from the available data. This curve was then utilized in determining the poison effects. There are nineteen isotopes, comprising a yield of 47%, that add considerable poison to the core system. Approximately 72% of the poison is contributed by isotopes of the rare earth group. Poison due to corrosion products also was appreciable. With one mil per year corrosion, these products are important when compared to the fission products. It thus can be seen that corrosion product removal would become as important as fission product removal if corrosion rates were as high as five mils per year. As accurate an analysis as is possible with the available data was made and the

results indicate the extent of reactor poisoning and the importance of core processing to remove these poisons. (auth)—NSA.   15285

8.4.5
Feasibility Study on a Shim Rod Facility Loop. Dynamic in-pile Loop Corrosion Testing. A. P. MILLER. Westinghouse Electric Corporation. U. S. Atomic Energy Commission Pubn., WAPD-CP-1505, October 14, 1955 (Declassified March 4, 1957), 17 pp. Available from Office of Technical Services, Washington, D. C.

A study was made to determine the feasibility of a MTR shim rod facility loop utilizing external loop equipment of the WAPD-13 dynamic corrosion loop. The necessary modifications are described in detail. Data are included on the decay of activated pressure tube and housing.—NSA.   15400

8.4.3, 5.2.1
External Casing Corrosion. Where Is It? How Bad Is It? J. D. SUDBURY. Continental Oil Co. *World Oil,* **144,** No. 6, 210, 212, 214, 217-218, 222 (1957) May.

Results of a series of casing potential surveys made in several wells in the San Miguelito field showed that external casing corrosion is due to an electrochemical mechanism as indicated by anodic slope of profiles. 3-5 amperes of impressed cathodic current was sufficient to remove all anodic slopes. Study of well Grubb 61 to determine how well potential profile defined zone of severe corrosion of casing, extent of damage at base of surface pipe and effect of cathodic protection on casing is described. Solid deposits found at various depths to 5200 feet included iron oxide film, mixture of iron carbonate and sulfide and calcium carbonate. Severe corrosion began at 2500 ft. and ended at 4600 ft. In all but two minor places, all corrosion penetration greater than 100 mils was in range of 2200-4600 ft. Crevice corrosion at collars occurred in this zone. All severe type corrosion was characterized by deep, rounded pits and a reddish-brown iron chloride as corrosion product with no traces of iron carbonate or sulfides. Presence of a thin calcareous deposit on casing indicated that cathodic protection was effective to depth of casing recovered. An applied current of 5 amperes is sufficient to prevent gross anodic corrosion in each well in this field. Diagrams, photos.—INCO.   14369

8.4.3
Fuel-Oil Additives: Fact and Fiction. J. F. SCOTT. *Marine Eng.,* **62,** No. 8, 75-77 (1957) July.

Modern refining technology has brought about drastic changes in petroleum processing in recent years. Today refineries obtain a gasoline and distillate yield of 85% compared to about 60% many years ago. However, fuel demands have increased continually, requiring use of lower quality crudes. Bunker C is a residual refinery product and crude-oil impurities naturally remain as contaminants in it. Many residual fuel oils available today contain larger concentrations of trouble-making impurities such as sulfur and vanadium compounds, sediment and water. These oils have a tendency to sludge badly. Effects of water in a fuel system include corrosion of tanks, pumps and lines and poor combustion. Description of tests showing effectiveness of different fuel oil additives is given. Photomicrographs, photos.—INCO.   15080

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8.4.3, 3.2.2, 1.7.1

Hydrogen Blistering in Cat Cracker Gas Plants. R. T. EFFINGER. Shell Oil Co. *Oil and Gas J.*, **55**, No. 41, 222, 224-225 (1957) Oct. 14.

Hydrogen blistering in catalytic cracker gas plants is limited to environments where water or sulfides exist and where high or low pH values prevail, according to a review of published literature and a questionnaire survey of the petroleum industry, conducted by the API Div. Refining Subcommittee on Corrosion. The attack occurs frequently in high pH or alkaline environments which are contaminated with cyanides and the more severe attacks generally follow the lighter hydrocarbon fraction through the plants. High nitrogen content in the feedstock increases the probability of hydrogen attack in the gas plants following catalytic cracking. Corrosion of this type, can be combated by improving feed preparation and controlling catalyst quality. The corrosive environment may be modified by water washing, dehydration, or inhibition. 15205

8.4.3, 3.4.7

Water Dependent Sweet Oil Well Corrosion Laboratory Studies. Reports of NACE Technical Unit Committee T-1C on Sweet Oil Well Corrosion (Joy T. Payton, Chairman). Compiled by Task Group T-1C-2 on Water Dependent Corrosion, Experimental Aspects (J. A. Rowe, Chairman). *Corrosion*, **13**, No. 11, 747t-749t (1957) Nov.

Extensive data are reported to show the correlation between bottom hole pH and tubing life under various production conditions. Data are given to show the following relationships: tubing life to calculated bottom hole pH for flowing gas lift sweet oil wells; tubing life to calculated bottom hole pH for gas lift sweet oil wells; produced iron and bottom hole pH for flowing, gas lift and pumping sweet oil wells and tubing life and produced iron in gas lift sweet oil wells. Total and average water production also are indicated for certain wells. 14426

8.4.3, 5.8.2

Status of Downhole Corrosion in the East Texas Field. A Report of NACE Technical Unit Committee T-1C on Sweet Oil Well Corrosion (Joy T. Payton, Chairman). Prepared by Task Group T-1C-5 on East Texas Field Corrosion (Harry G. Byars, Chairman). *Corrosion*, **13**, No. 11, 743t-746t (1957) Nov.

A report is made on the results of a "questionnaire" survey conducted to determine the status of downhole corrosion in the East Texas field. It was found that most of the companies involved felt that corrosion in East Texas varies from mild to severe depending on water production and well location. It was agreed that downhole corrosion presented a problem that could be combated economically with inhibitors. Although most of the operators had not been treating in East Texas long enough to compile full economic studies, data presented indicated that well maintenance cost could be reduced 60-90 percent by inhibition. Since a number of operators were still studying inhibition in East Texas, there was a wide variation in the types of chemicals used and in the treating schedules. Apparently, however, practically all good commercial inhibitors gave effective inhibition. 14409

The 15th Annual NACE Conference and 1959 Corrosion Show will be held March 16-20 at the Sherman Hotel, Chicago.

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The Western Region Conference is scheduled for September 29-30, October 1, 1959, at Bakersfield, Cal.

8.4.5

Corrosion Product Transport Study in the KAPL-37 Loop. F. C. STEINER AND F. J. WITT. Knolls Atomic Power Lab. U. S. Atomic Energy Commission Pubn., KAPL-M-SMS-89, December 23, 1957, 24 pp. Available from Office of Technical Services, Washington, D. C.

Experiments to study the transport of radioactive crud from contaminated out-of-pile surfaces to a newly installed precorroded pipe section in the KAPL-37 loop are described. The section installed formed a thimble by-pass. The radiochemical analyses of routine water and crud samples are tabulated and discussed.—NSA.   15406

8.4.5

Atomic Fuels. F. H. SPEDDING. Iowa State College. *Meta Progress,* 72, No. 4, 105-111 (1957) October.

Discussion of fuel element design considerations covers cost of fuel and fuel cycle, numerous variables in reactor design and planning of suitable fuel assembly for specific reactor, uranium and thorium fuels and nuclear physics upon which their reactions are based, radiation and corrosion effects. Materials used to can or coat fuel elements to prevent reaction with coolant solutions must have excellent thermal conductivity, but must not absorb too many neutrons. In homogeneous reactors, corrosion of pipes conducting

fluid is greatly enhanced; problem of mass transport can become very troublesome.—INCO.   15057

8.4.5

Recommended PBR Conceptual Design Program. J. E. MAHLMEISTER, W. H. HARKER, H. L. HOLLISTER, J. B. STICHKA AND E. D. KANE. California Research and Development Co. U. S. Atomic Energy Commission Pubn., LWS-22534, March 10, 1953 (Declassified February 15, 1957), 23 pp. Available from Office of Technical Services, Washington, D. C.

A study of the engineering limitations of the core design of the Argonne Power Breeder Reactor showed the Metallurgical limitations of high temperature materials, corrosive effects of plutonium, and thermal stresses to be the most severe. Preliminary specifications for solid fuel and liquid fuel reactors are included.—NSA.   15022

8.4.5

Homogeneous Reactor Project Quarterly Progress Report for Period Ending January 31, 1957. Oak Ridge National Lab. U. S. Atomic Energy Commission Pubn., ORNL-2272, April 22, 1957, 198 pp. Available from Office of Technical Services, Washington, D. C.

Homogeneous Reactor Test: Modifications were made of the differential-pressure and oxygen-metering systems.

During operation, difficulties were encountered with erratic diaphragm-pump performance, ruptured diaphragm valves and faulty construction. Metallurgical inspection showed that cracks in the leak-detector system were caused by stress corrosion from chloride impurity. Amsco 125-82 was recommended as the secondary refrigerant, replacing Freon 11. The 400 A-1 and 400 A-2 pump continued to circulate 0.04 M uranyl sulfate solution without difficulty. Testing operations of the HRT chemical processing plant was completed. Reactor Design and Analysis: Two-group, two-region nuclear calculations were extended for 10- and 12-ft-diam spherical reactors containing deuterium oxide-thorium dioxide-$U^{233}O_2$ in both core and blanket regions. Engineering Development: The high-pressure recombiner loop completed a run in which titanium and zirconium were exposed. Experimental and calculated detonation pressures in the hydrogen peroxide-water system are reported. A heat transfer system was constructed to check the validity of the Lawson heat transfer equation of slurries. A thorium dioxide-uranium dioxide slurry was prepared by simple mixing and circulated at 300 C in a 100 gpm loop. A 347 stainless steel valve was gold plated to improve corrosion resistance. Reactor Materials Research: Solution, slurry and radiation corrosion of reactor components in various media

are described. The stability of zirconium, niobium and titanium alloys at high-temperatures are discussed Chemical Engineering Development: Experiments on uranyl sulfate and thorium dioxide blanket processing are reported. Nine slurries of thorium dioxide were irradiated at 300 C in the LIRT and examined. Results are presented. Supporting Chemical Research: Temperatures of appearance of a second liquid phase were determined as a function of uranyl sulfate and copper sulfate concentrations in solutions. Results of experiments are reported for determining molecular and radical yield in deuterium oxide. Analytical Chemistry: Progress is reported in the development and improvement of methods for use in the analysis of HRT fuels.—NSA.   15030

8.4.5

Calculated Deposited Crud Activity in the PWR Primary System Due to Corrosion of Core Materials. F. W. PEMENT. Westinghouse Electric Corp.

U. S. Atomic Energy Commission Pubn., WAPD-PWR-CP-2995, April, 23, 1957, 19 pp. Available from Office of Technical Services, Washington, D. C.

The contribution of corrosion products of irradiated core materials to system contamination by particle deposition must be studied so that overall system contamination may be evaluated. The deposited crud forms, in effect, a background contamination which would be important in determining over-all system contamination resulting from, for example, failure of a few PWR blanket fuel rods. Corrosion of cobalt-bearing alloys in high flux region in the core is especially significant in this respect. The purpose of this report is to estimate the deposited activity in the PWR primary system of corrosion products from irradiated core materials. (auth.)—NSA.   14988

8.4.5

Reactor Water Processing: How It Is Done in APPR. A. L. MEDIN. Alco Products, Inc. *Nucleonics*, **15**, No. 12, 72, 74, 76, 78, 80-81 (1957) December.

Describes water-treatment facilities provided for Army Package Power Reactor. All construction materials in primary system are Type 304 stainless steel. With exception of Type 304 steam generator, conventional construction materials are used in secondary system. Corrosion products in APPR are primarily insoluble oxides of iron, nickel and chromium, although other impurities such as compounds of manganese and cobalt are also present. A micrometallic filter is located downstream of demineralizers to collect any resin leaving those units. The Type 304 filter elements remove all particles larger than 7 microns. Diagram.—INCO.   14994

8.8 Group 8

8.8.5

Choosing Alloys for Die-Casting. W. WOLF. *Metal Treatment*, **24**, No. 142, 272-276 (1957).

A concise review of tin, lead, zinc, aluminum, magnesium and copper-base pressure-die-casting alloys. The development of each alloy type is traced and comparisons made of the properties important to the die-caster (castibility, accuracy of finish, die attack, heat-checking tendency) and those required by the user (mechanical properties, machinability, corrosion-resistance and surface finish.)—MA.   15136

8.8.5

Where to Use Knitted Metal Parts. R. L. HARTWELL. Metal Textile Corp. *Materials in Design Eng.*, **46**, No. 1, 112-114 (1957) July.

Knitted metal mesh has a number of unusual properties that make it suited for a variety of applications. Unlike woven wire, knitted mesh is produced by interlacing loops of wire. Knitted wire gaskets of aluminum and Monel combine excellent conductivity with sufficient resiliency to provide tight joints with uneven mating surfaces. Although Monel is most corrosion resistant of materials used, galvanic corrosion in contact with aluminum raises questions concerning its use with aluminum enclosures. In practice, however, the mass of knitted Monel gasket is so much smaller than that of the aluminum that galvanic corrosion is minimized. Be-

cause of this effect, Monel shielding gaskets are used in contact with aluminum in much military electronic equipment. Material is called Goodloe packing. Photos.—INCO.   15297

8.9 Group 9

8.9.1, 3.5.8

Thermal Stresses and Thermal Buckling. J. SINGER, M. ANLIKER AND S. LEDERMAN. Polytechnic Institute of Brooklyn. U. S. Wright Air Development Center, U. S. Air Force, April, 1957, 120 pp. Available from Office of Technical Services, U. S. Dept., of Commerce, Washington, D. C. (Order PB 131072.)

Deals with aircraft structural problems arising from aerodynamic heating at supersonic speeds. Solutions relate to flat plate elements of the aircraft structure. The two major problems solved were the distribution of thermal stresses and the buckling of the flat plates under thermal stresses. Methods for the analysis of thermal stresses in plates of rectangular plan form and of constant or variable thickness are derived, discussed, and generalized to be valid in the case of a variable thickness. Recommendations are made for practical calculation of the thermal stresses. An experimental verification of the thermal buckling theory of the coverplates of multicellular supersonic wing structures is set forth. Experiments were conducted with an electromagnetic induction heater. Experimental results agreed well with predictions of the theory.—OTS.   15077

8.9.1, 3.5.8

Metallurgical Problems in the Aircraft Industry. J. FAGUET. *Rev. Met.*, **54**, No. 7, 555-568 (1957).

To obtain high specific mechanical properties in alloys used in aircraft manufacture it is necessary to consider characteristics affecting embrittlement under stress, fatigue and corrosion of the material and factors that may alter these characteristics. Improvements in creep properties of alloys at high temperature and under stress must not unduly affect plasticity; cermets present serious disadvantages in this respect. Difficulties encountered in deciding qualifications for materials used in very high-speed aircraft are described and heat properties are compared of 30 NCD steel, extrusion aluminum alloys A-U4GI and A-Z5GU and titanium alloys T-C3Fe, T-A4M and T-A6V. Cost of the materials is discussed.—MA.   14881

8.9.1

Status of High-Strength Steels for the Aircraft Industry. R. J. NEKERVIS, C. H. LUND AND A. M. HALL. Titanium Metallurgical Laboratory, Battelle Memorial Institute. January, 1958, 106 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121639).

Increased interest in steels shown by aircraft and missile manufacturers prompted this study of status of steel in the industry. Information is given on the kinds of steel available, the kinds in use, their properties, the aircraft and missile manufacturers' requirements and new developments in steel of potential interest to the aircraft and missile industry. Emphasis is placed on sheet steel for use in airframes, but other forms such as bar stock and forgings were also studied. Some non-airframe applications are also discussed.—OTS.   15166
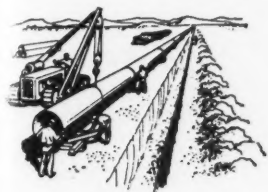
DURIRON

ANODE DATA SHEET

Basic engineering information about DURIRON impressed current anodes for cathodic protection.

Protection of a 30" Steel Water Line

Duriron Anodes Installed Without Backfill

THE PROBLEM: An isolated section of 11,000 feet of 30" steel water line needed cathodic protection. Tests showed the current requirements to be about 40 amperes, but it was planned to replace a section of the adjacent wood-stave line with steel, so extra capacity was desired. Only one site, about 4000 feet from one end of the section, had a power supply available. The ground at this location was a peat bog, with a resistivity of 4000 ohm-centimeters. The water table stood within six inches of the surface, making it impossible to get a dry, clean hole for the installation of anodes.

THE INSTALLATION: Thirty-two Duriron Type D anodes (2" x 60") were used, without backfill (Fig. 1). They were installed by digging through the dry surface soil for about one foot, and then pushing the anodes down until the tops were three feet below the surface (Fig. 2). The calculated resistance for the thirty-two anode group, at twenty foot spacing in two rows, was one ohm, based on previous experience with similar installations. Had it been possible to install anodes in conventional backfill columns, the requirements could have been met with twenty-two anodes. Under the circumstances, the use of bare anodes effected a considerable saving.
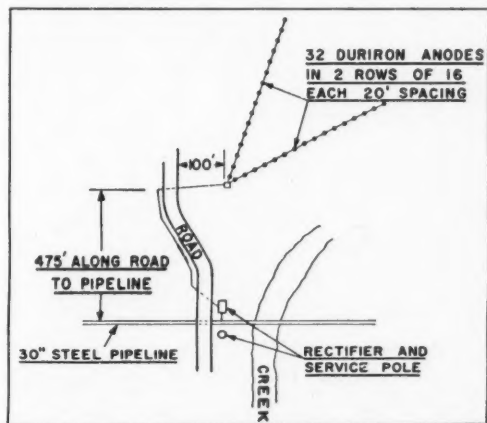
THE PERFORMANCE TO DATE: The anode bed is discharging 60 amperes at a terminal voltage of 59 volts. The entire line section is under protection, the minimum potential being 1.18 volts (referred to a copper-copper sulfate electrode placed over the line). This affords ample margin to handle anticipated additions to the line. It should be noted that the calculated anode resistance $R = .005\rho$ is quite close to the actual resistance of $R = .00491\rho$.
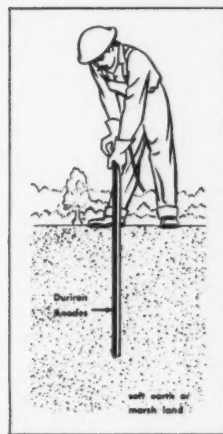

Fig. 2—Method of installing anodes

Fig. 1—Illustration of anode spacing

THE DURIRON COMPANY, INC.
Dayton 1, Ohio